Organic Analytical Reagents

VOLUME TWO

BY

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TO MY FATHER

whose clear vision and deep understanding have contributed so much to the preparation of this work.

PREFACE

Since the earliest days of analytical chemistry, organic reagents have been employed in various ways to facilitate the detection and determination of chemical substances. Only during the past two or three decades, however, have these compounds been used extensively in analytical procedures. At present they are rapidly gaining in popularity because of their greater sensitivity and specificity as compared to inorganic reagents, and also because of the greater convenience with which they may be employed in many analytical procedures.

The principal purpose in preparing this book has been to assemble in one place a description of all organic compounds used in the analysis of inorganic substances, and to present a discussion of the methods employing these reagents.

The information used in this book is taken from all publications appearing prior to January 1, 1946. Due to conditions resulting from the war, foreign journals have been delayed or prevented from reaching the United States, and in consequence much of the material contained in the more recent publications has been taken from *Chemical Abstracts.* For this reason, not all articles published before January 1, 1946, have been reviewed. The chemist who uses this book in reviewing the literature may, however, be guided by this principle: that all articles appearing in *Chemical Abstracts* up to and including 1945, as well as all original journals available to this date, have been included.

References to the literature have been made so as to indicate, at least to some extent, the subject matter of each. Thus the chemist who wishes to use a certain reagent for a given purpose has available a comment on almost every article that has been written on the subject and, in addition, the reference to the original publication in the event he wishes to consult this source. In this connection, it may be helpful to note that bibliofilm or photostat copies of articles appearing in most chemical journals can be secured at moderate cost from the United States Department of Agriculture Library, Washington, D. C.

Many obviously inferior reagents and methods are included since the treatment of the subject is intended to be complete. The inclusion of inferior methods is justified because of two considerations: in the future no time need be lost in attempting analytical methods that in the past have been demonstrated as unsatisfactory; and further, an inferior method may, with suitable modifications, be made useful for certain purposes.

In order to promote a more comprehensive study and a wider use of organic compounds in inorganic analysis, methods have been included for the preparation of most compounds listed in the book. For most substances, several methods appear in the literature and, in selecting the one to be included, the author has been guided by the principle that it be the most adaptable in the average chemistry laboratory. It should be stated that only a few of the methods of synthesis described have been used by the author, and undoubtedly some may prove unsatisfactory. Consequently, any information regarding better methods is earnestly solicited.

The primary aim of this book has been to collect in one place all information relating to the analytical uses of a given compound, and this principle has been adhered to regardless of structural characteristics or analytical functions. In a classification based on functions alone, many compounds would necessarily appear in different sections. For example, benzidine is used as a reducing agent, a basic salinogenic compound and in diazotization and coupling reactions for nitrite. Further, any classifications based upon functional groups present in the organic molecule would be somewhat arbitrary, since many compounds possess more than one group which affects their chemical reactions. The plan finally adopted calls for the complete treatment of each compound in one section, since any disadvantage resulting from this lack of regard for function and structure is believed compensated by the convenience of localization of information. In general, chemically related compounds are grouped together in so far as this is practicable; thus, the alcohols, amines, acids, oximes, arsonic acids, etc., form separate sections. It must be emphasized that owing to the diverse character of the reagents used in analytical procedures the associations of these substances in separate sections of this book may be somewhat debatable from the purely chemical point of view, but the plan used here seemed to be the most practicable that could be devised by the author. Although this scheme may separate such substances as reducing agents or oxidizing agents through widely scattered parts of the book, every reference to a particular reagent will be found in the section devoted to that compound.

The author is painfully aware of the many inconsistencies and ambiguities which appear in various parts of this book. Contradictory claims made by various authors are purposely included in order that the analyst may properly evaluate their merit through additional research. Many vague descriptions of methods and procedures are presented simply because the original sources themselves are not clear. Frequently, too, in translations or in abstracts errors have been discovered, which indicates too clearly that many more must certainly have escaped notice. The possibility of any error, or incompleteness of description has not prevented inclusion of certain important material, since such omissions would lead to incomplete coverage of some topics. The author also realizes that he must accept the responsibility for many mistakes, and he earnestly hopes that these will be communicated to him.

Another source of error has appeared in many publications: due to the character of chemical nomenclature, often there has been some doubt as to exactly what compound is referred to in certain discussions. This is especially true of the dyes, but is true also of certain other compounds. Every effort has been made to see that these references have been properly evaluated.

Indianapolis, Ind.
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F. J. W.

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CHAPTER I

THE ORGANIC ACIDS

Many organic compounds exhibit acidic properties, but in this section only those are included which contain the carboxyl group. These substances are especially valuable in neutralization reactions and in the preparation of buffer solutions, but many possess additional properties which make them useful in analytical chemistry. For example, certain carboxylic acids are used for the precipitation of insoluble normal salts, such as the oxalates of calcium, barium and strontium, and also for the conversion of certain ions into soluble complexes, such as that of aluminum with tartaric acid. Some organic acids are also useful as reducing agents, such as oxalic acid in the reaction with the permanganate ion. Properties of precipitating action, complex formation and reduction are more or less specific for individual members of the group of acids, but the so-called acidic properties are to some extent common to all.

The effective use of organic acids in the control of acidity in analytical procedures requires a general knowledge of the fundamental concept of acids and bases. While it is impossible here to develop in detail the theory of acidity, a review of a number of the more important principles will prove helpful in providing the basis for many useful practical calculations.

An acid may be defined as a substance which yields protons or hydrogen ions. A great many dissimilar substances fall into this classification, such as the ammonium ion, hydrogen chloride, acetic acid, the hydronium ion and the bicarbonate ion. While these substances differ markedly from one another in their general properties, they all exhibit the characteristics of acids because of their common tendency to yield hydrogen ions in solution.

Acids differ widely in the extent to which they are ionized in aqueous solutions. Many, such as hydrogen chloride, hydrogen bromide, hydrogen iodide, perchloric acid, nitric acid, sulfuric acid, hydroferricyanic acid and the organic sulfonic acids are completely ionized with negligible quantities, if any, of the unionized molecular compound remaining. These are termed *strong acids.* Others, which include the organic acids, are only slightly ionized in aqueous solution, and are called *weak acids.*

Available evidence indicates that the hydrogen ion in solution is solvated to form what might be termed a solvonium ion. Thus, in an aqueous solution of an acid the hydrogen ion is hydrated to form the hydronium (or oxonium) ion, H_3O^+, and it is this ion which is responsible for the so-called acidic properties. For simplicity in the following discussion, however, the classical symbol for the hydrogen ion, H^+, is used with the understanding that it is always present in the hydrated form in aqueous solution.

The organic acids, as well as other weak electrolytes, ionize reversibly according to the equation

$$HA \rightleftarrows H^+ + A^- \tag{1}$$

where HA is the acid and A^- the anion of the acid. Applying the principle of equilibrium and the law of mass action, the following equation is obtained

$$\frac{[H^+] \times [A^-]}{[HA]} = K_A \tag{2}$$

in which $[H^+]$ and $[A^-]$ represent the molar ionic concentration of the hydrogen ion and anion respectively and $[HA]$ is the molar concentration of the unionized molecules. K_A is a constant at any definite temperature.

Since the magnitude of K_A is determined by the concentration of the ions and unionized molecules, this value is a most useful index of the extent of ionization of an acid. The ionization constants of a number of organic acids are shown in Table 1. Not only are these constants useful to indicate relative strengths of acids, but they are also valuable in the solution of a number of problems of practical importance in analytical chemistry.

The molar concentration of an organic acid in aqueous solution is quite different from the concentration of the hydrogen ion, since these acids are weak acids and only incompletely ionized. The actual hydrogen ion concentration may be determined experimentally by several methods, but in many cases it is helpful to calculate the ion concentration without employing the more difficult and time-consuming experimental procedure. From equation (1) it is seen that in a solution containing only an acid which yields one hydrogen ion and one anion upon the ionization of one molecule, $[H^+] = [A^-]$ and $[HA] = c - [H^+]$, where c is the molar concentration of the acid. Consequently equation (2) becomes

$$\frac{[H^+]^2}{[HA]} = K_A \text{ or } \frac{[H^+]^2}{c - [H^+]} = K_A \tag{3}$$

and

$$[H^+] = -\frac{K_A}{2} + \sqrt{\frac{K_A^2}{4} + K_A c} \tag{4}$$

For many weak electrolytes, $[H^+]$ is so small compared with c that $c - [H^+]$ becomes virtually equal to c; hence, an approximate form for equation (4) can be written

$$[H^+]^2 = K_A c \tag{5}$$

or

$$[H^+] = \sqrt{K_A c} \tag{6}$$

This form of the equation can be used with negligible error if $[H^+]$ is less than about 5 per cent of c, but if $[H^+]$ is greater than 5 per cent of the acid concentration, the exact equation (equation (4)) should be used.

A careful control of the acidity of solutions is often important in precipitation reactions and in effecting many analytical separations. The optimum conditions of acidity and alkalinity are generally expressed in terms of pH, which is defined by the equation

$$pH = -\log H^+ \qquad (7)$$

TABLE 1.—IONIZATION CONSTANTS OF ORGANIC ACIDS (25° C.)

Acid	K (First Hydrogen)	K (Second Hydrogen)
Acetic	1.86×10^{-5}	
Alanine	9×10^{-10}	
Barbituric	1.05×10^{-4}	
Benzoic	6.6×10^{-5}	
Bromoacetic	1.38×10^{-3}	
α-Bromopropionic	1.08×10^{-3}	
β-Bromopropionic	9.8×10^{-5}	
Butyric	1.48×10^{-5}	
Chloroacetic	1.55×10^{-3}	
α-Chloropropionic	1.47×10^{-3}	
β-Chloropropionic	8.59×10^{-5}	
Citric	8×10^{-4}	
Crotonic	2.0×10^{-5}	
Formic	2.14×10^{-4}	
Fumaric	1×10^{-5}	3×10^{-5}
Hippuric	2.3×10^{-4}	
Isobutyric	1.5×10^{-5}	
Isovaleric	1.7×10^{-5}	
Lactic	1.55×10^{-4}	
Maleic	1.5×10^{-2}	2.6×10^{-7}
Malic	4×10^{-4}	9×10^{-6}
Malonic	1.61×10^{-3}	2.1×10^{-6}
Mandelic	4.29×10^{-4}	
Mucic	6.3×10^{-4}	
α-Naphthoic	2×10^{-4}	
β-Naphthoic	6.8×10^{-5}	
Nicotinic	1.4×10^{-5}	
Oxalic	3.8×10^{-2}	4.9×10^{-5}
Phthalic	1.26×10^{-3}	3.1×10^{-6}
Picolinic	3×10^{-6}	
Pyromucic	7.1×10^{-4}	
Salicylic	1.06×10^{-3}	1×10^{-13}
Succinic	6.6×10^{-5}	2.8×10^{-6}
Sulfanilic	6.2×10^{-4}	
Tartaric	1.1×10^{-3}	6.9×10^{-5}
Tartronic	5×10^{-3}	
Trichloroacetic	2×10^{-1}	
Valeric	1.6×10^{-6}	

Since $[H^+] = \sqrt{K_A c}$, the pH of a pure aqueous solution of an organic acid may be calculated from the equation

$$pH = -\tfrac{1}{2} \log K_A - \tfrac{1}{2} \log c \qquad (8)$$

where K_A is the ionization constant and c the molar concentration of the acid. Since c as used in this equation is the molar concentration of the acid and not the actual concentration of the unionized acid molecules, the value of pH so obtained is only approximate, but it is sufficiently accurate for most practical purposes if the degree of ionization does not exceed 5 per cent. This method also gives a fair approximation for dibasic acids if the first ionization is used.

Solutions used in most analytical procedures contain not only the free acid but also some of the salt of the acid. In this case $[H^+]$ and $[A^-]$ are not the same, but $[H^+]$ may be calculated by the equation

$$[H^+] = \frac{K_A c}{[A^-]} \qquad (9)$$

and

$$pH = -\log K_A - \log c + \log A^-$$

An approximate value of pH may be calculated if c is taken as the molar concentration of the acid and $[A^-]$ as the concentration of the salt. This equation is very useful, since buffer solutions are very important in analytical chemistry. When c and $[A^-]$ are equal

$$pH = -\log K \qquad (10)$$

Another problem of importance is the calculation of the approximate pH of a simple solution of a salt of a weak acid and a strong base. This may be obtained from the equation

$$[H^+] = \sqrt{\frac{K_W \times K_A}{[A^-]}}$$

in which K_W and K_A are the ionization constants of water and the weak acid respectively, and $[A^-]$ is the molar concentration of the salt. Then

$$pH = 7 - \tfrac{1}{2} \log K_A + \tfrac{1}{2} \log [A^-].$$

A description of a number of the more important organic acids is included in the following sections:

ACETIC ACID

$C_2H_4O_2$ Mol. Wt. 60.05 Beil. Ref. II, 96.

CH_3CO_2H

Use: Detection of beryllium and sodium.

Determination of aluminum, chromium, cobalt, iron, manganese, sodium, titanium and zirconium.

Acetic acid is a colorless liquid of pungent odor. Its sp. gr. is 1.049. It boils at 118.1° C. and solidifies at 16.7° C. It is miscible with water, alcohol, and ether, but it is insoluble in carbon disulfide and carbon tetrachloride. Its dissociation constant at 25° C. is 1.86×10^{-5}

The most important use of acetic acid in analytical work is for the neutralization of solutions, and for the preparation of buffers. It is the most commonly used of all weak acids in laboratory procedures.

The basic acetate method for the separation of sesquioxides from protoxides in the third analytical group is also a very important use of acetic acid. Sodium acetate is an important reagent for the reduction of the hydrogen ion concentration of solutions of mineral acids through the conversion of highly ionized mineral acids to slightly ionized acetic acid.

Acetic acid is also an important solvent for many organic compounds in various analytical procedures. For example, diphenylamine, diphenylbenzidine, and 8-hydroxyquinoline are used in acetic acid solutions. Acetic acid is also used as a solvent in certain separations. For example, uranium dissolves in a mixture composed of 20 parts of acetic acid and 5 parts of nitric acid, while vanadium does not.[197] Many metals, antimony and tin excepted, and their alloys dissolve in 50 per cent acetic acid and 30 per cent hydrogen peroxide, and the resulting solutions are particularly well suited for further analytical treatment.[198]

Detection and Determination of Sodium

Under properly controlled conditions sodium can be precipitated as a slightly soluble triple acetate with the uranyl ion having the general formula:

$$Na(C_2H_3O_2) \cdot M(C_2H_3O_2)_2 \cdot 3UO_2(C_2H_3O_2)_2 \cdot 6H_2O$$

in which M may be magnesium, zinc, nickel, cobalt, manganese and certain other divalent metals. The most satisfactory reagents for the sodium precipitation are formed with zinc and magnesium.[18] Streng [1,2] first discovered that sodium is precipitated with uranyl acetate, or as the triple salt of sodium magnesium uranyl acetate. Blanchetiere [4] studied the work of Streng and determined the composition of the sodium salt formed with magnesium uranyl acetate. Kolthoff [5] used this reaction as a qualitative test for sodium, and later Kling and Lassieur [6] applied the reaction to a quantitative method for the determination of sodium. This method has been extensively studied and much of this work has been reported in a number of excellent reviews[44,51,60,61,68,92,98,127,145,153,188,201].

The following procedures, due to Kolthoff,[5,75] illustrate the use of uranyl acetate reagents for the detection of sodium.

(a) Magnesium uranyl acetate:

Reagent. Dissolve 10 g. of uranyl acetate and 6 g. of 30 per cent acetic acid in water and dilute to 50 ml. Dissolve 33 g. of magnesium acetate and 6 g. of acetic acid in water and dilute to 50 ml. Mix the two solutions and allow to stand for several days. Filter and use the clear filtrate.

Procedure. Add 10 drops of the reagent and 2 ml. of alcohol to 2 ml. of the solution to be tested. A turbidity or precipitate forms within one hour if the concentration of sodium is greater than 50 mg. per liter.

(b) Zinc Uranyl acetate:

Reagent. Dissolve 10 g. of uranyl acetate and 6 g. of 30 per cent acetic acid in 34 g. of water. Heat, and mix the hot solution with a hot solution prepared by dissolving 30 g. of zinc acetate and 3 g. of acetic acid in 17 g. of water. Allow to stand one day and filter.

Procedure. Mix 4 ml. of the reagent with 0.5 ml. of the solution to be tested. A crystalline precipitate forms at once or after some time, depending on the amount of sodium present. The precipitate forms within 30 minutes with as little as 50 mg. of sodium per liter. The test is made more sensitive if alcohol is present.

A great many modifications of uranyl acetate reagent have been proposed from time to time in an effort to improve the sodium separation. The more important of these are listed in the following sections:

Magnesium uranyl acetate. Many investigators have employed magnesium uranyl acetate for the precipitation of sodium.[1-22,29-31,36,37,42,45,49,63,65,69,127,225,226] Many have used the reagent originally proposed by Blanchetiere,[4,6,7,9,14-16,19,127] which has the following composition:

Solution a	*Solution b*
Uranyl acetate 100 g.	Magnesium acetate 333 g.
Glacial acetic acid 60 g.	Glacial acetic acid 60 g.
Dilute with water to 1 liter	Dilute with water to 1 liter.

This reagent has been modified as follows:

(a) The same quantity of salts have been dissolved in sufficient water to form only one-half the final volume described above.[5,11,49]

(b) The amount of crystalline uranyl acetate has been reduced to 85 g. and the magnesium acetate increased to 500 g.[17,18,20,22,36,42]

(c) The quantity of uranyl acetate dihydrate has been decreased to 90 g. and the magnesium acetate tetrahydrate has been increased to 600 g.[21,30,31,65]

(d) The amount of magnesium acetate tetrahydrate has been increased to 700 g.[29]

(e) A special reagent may be prepared by dissolving 25 g. of uranyl acetate, 150 g. of magnesium acetate and 780 ml. of glacial acetic acid. With this reagent it is claimed that there is no error due to potassium or lithium.[40,127] This same reagent has been diluted with an equal volume of water.[44]

The following special reagent has also been prepared:[127]

Solution a	*Solution b*
Uranyl nitrate—10 g.	Magnesium acetate—30 g.
30% acetic acid—6 ml.	30% acetic acid—3 ml.
Dilute to 65 ml. with water.	Dilute to 65 ml. with water.

This reagent gives a nitrate-free triple acetate.

Many authors have recommended the use of an alcoholic solution of magnesium uranyl acetate.[28-25,27,28,82,88,85,89,41,48,50-62,55,57-59,66-68,70,127]. The following reagent has been proposed by Kahane[24,25]:

Uranyl acetate (cryst.)	32 g.
Magnesium acetate	100 g.
Glacial acetic acid	20 ml.
90% ethyl alcohol	500 ml.

Dilute with water to one liter.

Liegeosis[127] claims that in using this reagent for the determination of sodium an error occurs due to the precipitation of uranyl oxide. Caley and coworkers[48] have used a similar reagent containing 30 g. of uranyl acetate dihydrate, 150 g. of magnesium acetate tetrahydrate and an equal quantity of 95 per cent ethyl alcohol. Canessa[47] has increased the uranyl acetate to 35 g. and magnesium acetate to 150 g. Nydahl[59] recommends the following formula for the sodium reagent:

Uranyl acetate	19 g.
Magnesium turnings	25.5 g.
Glacial acetic acid	85 ml.
6 N Hydrochloric acid	165 ml.
95% Ethyl alcohol	500 ml.

Dilute with water to 1 liter.

Zinc uranyl acetate. Many analysts have proposed formulas for the uranyl acetate reagent in which zinc is substituted for magnesium.[8,26,44,46,78-77,79-82,84,86-88,90,91,98-96,98,101-100,108,112-114,116-120,128-125,127-129,131,188-145,148,149,161,158,154,156,157,161-164,166-168,170,171,178,174,204-206,227] The following reagent has been proposed by Barber and Kolthoff,[76] and others:

Solution a	*Solution b*
Uranyl acetate dihydrate—10 g.	Zinc acetate trihydrate—30 g.
30% acetic acid—6 g.	30% acetic acid—3 g.
Dilute with water to 65 g.	Dilute with water to 65 g.

The following modifications of this reagent have been proposed:

(a) Some authors recommend the addition of 50 ml. of water instead of diluting to 65 g.[74,79,141,162,167,174]

(b) The quantity of zinc acetate may be increased by about 50 per cent[117] and the uranyl acetate by approximately 20 per cent.[88,118,116]

(c) The amount of acetic acid may be increased to 60 ml. and the quantity of water to 320 ml.[187] In this formula the glacial acetic acid may be reduced to 20 ml.[128]

(d) A similar reagent may be prepared containing 1.5 per cent alcohol with a final volume of only 50 ml.[85]

(e) Broadfoot and Browning[168] add 15 ml. of nitric acid to each 100 ml. of reagent to reduce coprecipitation.

(f) The reagent of Barber and Kolthoff may be used after diluting with an equal amount of alcohol.[93,99,100,109]

(g) Sassier[132] has used a reagent similar to that of Kahane's.

DETERMINATION OF SODIUM

The methods used for the final determination of sodium with the aid of uranyl acetate are very numerous, but all of these depend upon the precipitation of sodium from an aqueous solution as the slightly soluble triple acetate. The sodium precipitate may be weighed directly after drying or upon ignition as a gravimetric procedure, or it may be determined titrimetrically or colorimetrically.

(a) **Gravimetric determination.** The quantity of water of hydration contained in the triple acetate precipitate has been the subject of considerable controversy. Some state that the magnesium precipitate contains 9 molecules of water, while others claim that when an alcoholic solution of the reagent is used only 8 molescules of water are present. Six molecules is the number usually employed in the calculation, although according to some the number is more nearly 6.5.

The water content of dried sodium zinc uranyl acetate is slightly greater than that corresponding to the hexahydrate. Schoorl[67] reports that the amount of water depends upon the humidity of the atmosphere in which the precipitate is dried. The water content reported after drying in air at various humidities and at room temperatures is given in Table 2. The water of hydration of the triple acetate is not expelled when the precipitate is heated at 110° C.

TABLE 2.

Relative Humidity Per Cent	Moles of H_2O in Precipitate
0.	6.17
0.34	6.45
0.68	6.53
0.94	6.64
0.98	6.80

The precipitate is weighed in the air-dry state as the hexahydrate. The slight error which results from regarding the precipitate as the hexahydrate is compensated by small solubility losses in the procedure.

The solubility of sodium zinc uranyl acetate is 5.85 g. per 100 ml. of solution at 21° C., and this is fairly high for a quantitative precipitation. Special precaution, therefore, must be taken to insure the complete separation of sodium. This can be accomplished by adding a comparatively large volume of a concentrated solution of zinc uranyl acetate, which is saturated with the sodium salt, to a very small volume of the solution of the sodium salt. Precipitation occurs immediately, but the mixture should be allowed to stand for an hour or more with occasional stirring to insure quantitative separation. After collecting the precipitate on a filter crucible, it is washed with successive small portions of the reagent solution that has been saturated with the triple salt. The wash solution is then removed with 95 per cent alcohol that is saturated with sodium zinc uranyl acetate, and finally the precipitate is washed with acetone or ether to remove the alcohol. The sodium factor is 0.01495. The smallness of the factor is a great advantage when a small quantity of sodium is determined, but it limits the weight of sample that can be used when sodium and potassium are present in similar quantities. The following procedure is recommended by Barber and Kolthoff,[76] and this may be taken as typical of the gravimetric sodium procedures:

Reagent. *Zinc uranyl acetate. Solution a:* Mix 10 g. of uranyl acetate, $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$, 6 ml. of 30 per cent acetic acid and 50 ml. of water and warm until solution is complete.

Solution b: Mix 30 g. of zinc acetate, $Zn(C_2H_3O_2)_2 \cdot 2H_2O$, 3 ml. of 30 per cent acetic acid and 50 ml. of water and warm until all the solid has dissolved.

Mix equal volumes of solutions *a* and *b* and allow the mixture to stand for 24 hours. If a precipitate forms, due to the presence of small quantities of sodium salts, filter and store the solution in a pyrex bottle. If no precipitate forms, add a small quantity of sodium chloride in order to saturate the solution with the sodium salt. Filter and store in a pyrex bottle.

Procedure. Dissolve a sample containing not more than 8 mg. of sodium and 25 mg. of potassium in 1 ml. of water and add 10 ml. of the zinc uranyl acetate solution. Mix and allow to stand for one hour. Stir occasionally to insure complete precipitation. Filter through a filtering crucible, and remove as much of the solution as possible with suction. Wash the beaker in which the precipitation was carried out, the crucible and the precipitate with five to eight 2-ml. portions of the reagent and allow the precipitate to drain each time. Then wash five times with 2-ml. portions of 95 per cent alcohol that has been saturated with sodium zinc uranyl acetate at room temperature, and then wash with a few small portions of ether or acetone. Draw air through the crucible for a few minutes to remove the ether or acetone and place the crucible in the balance case. Allow to stand for 10-15 minutes and weigh. Allow to stand in the balance case for an additional 10 minutes and again weigh to be sure the weight is constant. The weight of sodium is found by multiplying the weight of the precipitate by 0.01495. This method is accurate to about 0.5 per cent.

When the precipitates are ignited and weighed the following factors are used:[127]

Ignited Precipitate	Sodium Per Cent	Na_2O Per Cent
$(U_2O_7Mg)\frac{1}{2}(U_2O_7Na_2)$	2.474	3.334
$(U_2O_7Zn)\frac{1}{2}(U_2O_7Na_2)$	2.369	3.193

Lithium interferes in the above determination, since this metal also forms a slightly soluble triple acetate. Caley and Rogers[209] have prepared a reagent which is not very sensitive toward lithium, but which unfortunately is not very sensitive toward sodium. This reagent has the following composition:

Uranyl acetate $(UO_2(C_2H_3O_2)_2 \cdot 2H_2O)$	88 g.
Cupric acetate $(Cu(C_2H_3O_2)_2 \cdot 2H_2O)$	88 g.
Glacial acetic acid	60 ml.

Sufficient water to make 1 liter of solution.

Better results are obtained by replacing a part of the water with ethyl alcohol. The best mixture for use in the presence of lithium has the following composition:

Uranyl acetate $(UO_2(C_2H_3O_2)_2 \cdot 2H_2O)$	40 g.
Cupric acetate $(Cu(C_2H_3O_2)_2 \cdot 2H_2O)$	20 g.
Glacial acetic acid	100 ml.
Ethyl alcohol	500 ml.
Water	450 ml.

The precipitate formed with this reagent appears to have the composition: $3UO_2(C_2H_3O_2)_2 \cdot Cu(C_2H_3O_2)_2 \cdot NaC_2H_3O_2 +$ approx. $5H_2O + 1.5\ C_2H_5OH$. From 1-50 mg. of sodium can be determined satisfactorily by assuming that the precipitate dried at 60° C. contains 1.45 per cent sodium. Lithium causes a slight positive error.

Potassium does not interfere except when present in relatively large quantities. Dworzak and Liebenberg[58] say that the limit of allowable potassium is 2:1. Others[83,95,107] place the limit at 20:1, while Japhe[136] states that this may be as high as 100:1. Mulwani and Pollard[130] say that the ratio of potassium to sodium may be 12:1 for titrimetric methods but only 4:1 for colorimetric methods.

Phosphates yield precipitates with the reagent and must be removed. Protein, albumin and other organic materials may also interfere. Ammonium salts, magnesium, calcium and barium may be present in moderate quantities without interference although strontium causes high results. Chromium may interfere. Antimony, mercury and silver, as well as oxalates and arsenates also interfere. Aluminum, lead, manganese, cobalt, cadmium, nickel, cesium and rubidium do not interfere. Molybdate interferes with the formation of precipitates with zinc uranyl acetate reagents. The error is sometimes positive and sometimes negative depending upon whether the precipitate is retained on the filter or not. By the addition of tartaric or citric acid, however, a complex anion containing molybdenum is formed which does not contaminate the sodium precipitate noticeably.

Sulfate must be absent when potassium is simultaneously present, since potassium sulfate is only slightly soluble in the reaction mixture.

Titrimetric determination of sodium. Many investigators have determined sodium titrimetrically after precipitating as sodium zinc (or magnesium) uranyl acetate [10,20,23-25,31,34,48,51,52,59,70,84,88-90,96,99,100,104,106,109,110,113,115-117,119,120,122,127,130,132,135,139,142,143,147,149,172]. Many of these methods are based upon the reduction of hexavalent uranium in the precipitate to the tetravalent state, and the subsequent titration of U(IV) → U(VI) with the aid of various oxidizing agents. Potassium permanganate,[10,23-25,31,34,51,52,59,90,96,116,119,120,127,135,149] ceric sulfate,[31,59,110,122,139] and potassium dichromate[104,117] have been used as the oxidizing agents.

Blenkinsop[84] recommends adding potassium thiocyanate to the uranium solution that has been reduced with titanium trichloride, and titrating the excess titanium trichloride with ferric potassium sulfate to a red end-point.

An iodometric method has been employed which is based upon the following steps: Dissolve the precipitate, add ammonium sulfate, sulfuric acid, potassium iodide, and starch and then gradually add potassium ferricyanide, and finally titrate the liberated iodine with a standard thiosulfate solution.[106]

Caley[20] dissolved the precipitate in acetic acid and titrated the uranium with a standard disodium phosphate solution. This method has been modified by adding an excess of standard disodium hydrogen phosphate and back titrating the excess with uranyl acetate,[99,100,109] using cochineal as indicator.

Arnoux and Coulomb[70] dissolved the sodium precipitate in a sodium acetate solution, heated the mixture to boiling and then precipitated the uranium as red $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ with the aid of 8-hydroxyquinoline. This precipitate was then dissolved in dilute hydrochloric acid, an excess of standard potassium bromate added and the excess determined by the addition of potassium iodide and subsequent titration with standard thiosulfate.

Dulac and Bouat[48] determined sodium indirectly by estimating the amount of acetate in the sodium precipitate. They treated the sodium precipitate with tartaric acid, removed the acetic acid by steam distillation and titrated the distillate with barium hydroxide. The acetate content of the precipitate may also be determined by adding an excess of standard sodium hydroxide to the precipitate and titrating the excess with standard hydrochloric acid to an end-point with phenolphthalein.[88,116,182] Several investigators have recommended titrating the precipitates directly with standard sodium hydroxide.[89,113,115,142,143,172]

Colorimetric determination of sodium. Many methods have been proposed for the colorimetric determination of sodium after precipitation as the triple acetate.[15,18,22,25,26,33,38,49,69,72,74,81,85,93,97,101,108,111,114,125,130,134,137,141,153,154,156,157,170,182,184]

One of the most widely used methods for the development of a color in solutions of the sodium precipitate is based upon the conversion of the uranyl radical to reddish-brown uranyl potassium ferrocyanide ($UO_2K_2Fe(CN)_6$) by the addition of potassium ferrocyanide. This reaction has been studied by many investigators.[15,25,26,38,74,81,85,93,101,108,111,114,130,141,153,150,157,170] The color is independent of acidity in solutions ranging from 0.4 to 5.0 per cent acetic acid. A 2 per cent acetic acid concentration has been recommended.[111,153] The reaction does not take place in an alkaline medium. An optimum color is developed with a 0.2 per cent solution of a uranium salt and a 1 per cent solution of potassium ferrocyanide.[15] With greater quantities of potassium ferrocyanide, the color is increased.[88] The color is proportional to the sodium content of the solution within a range of 50 per cent variation between the standard and sample solution.

Ernst and Barasits [81] recommend adding an excessive quantity of acetic acid to stabilize the color. Tissier and Benard [15] claim that with high concentrations of potassium ferrocyanide a precipitate may form. Marenzi and Vilallonga [170] report that a turbidity may result with the ferrocyanide method, and suggest using a 1 per cent solution of sodium bisulfate as a stabilizing agent.

The following method may be used for the determination of small quantities of sodium.

Procedure. Dissolve the precipitate of sodium zinc uranyl acetate, formed as described above, in 10 ml. of water and transfer to a 25-ml. volumetric flask. If the sodium concentration is relatively large, the sample solution should be diluted to a larger volume. In a similar flask, place the precipitate which is formed from 1 ml. or more of a standard sodium chloride solution, and to both sample and standard add 1 drop of glacial acetic acid and 0.5 ml. of 20 per cent potassium ferrocyanide for each 25 ml. of final volume. Dilute to the mark, mix well, and compare the resulting colors after three minutes.

In the presence of large quantities of potassium, dilute the solution of the sample so that the potassium content does not exceed 0.3 mg. per ml. Then add 0.5 ml. of 7 per cent potassium ferrocyanide and 1 drop of glacial acetic acid to each 7.5 ml. of the sample solution. The resulting color is compared with a standard similarly prepared.

The standard sodium solution is prepared by dissolving 0.1271 g. of pure sodium chloride in water and diluting the resulting mixture to 1 liter. Add a few ml. of chloroform as a preservative. One ml. of this solution contains 0.05 mg. of sodium.

A number of methods are based upon the use of the normal color of the sodium triple salt for comparisons against standards.[18,22,36,69,97] Standards are prepared in the same manner as the unknown, and are stable for about one month.[86] In making the comparison, the temperature of the sample and the standard must be the same.[18] Alcohol must not be added to the final solution in making the color comparison, since otherwise an error results due to precipitation of the triple salt.[22,97]

The following procedure may be used for the direct comparison:

Procedure. Dissolve the precipitate of the sodium triple salt by adding water warmed to 60-70° C. in 2-ml. portions until solution is complete. Collect the solution in a comparison tube and allow to cool. Dilute to a standard volume, depending upon the intensity of the color, and compare with a standard similarly prepared, using 2 ml. of standard sodium chloride solution. If more than 5 mg. of sodium is present in the sample, the colorimetric method should not be used, but rather the sodium should be determined gravimetrically.

When sodium zinc uranyl acetate is dissolved in a solution of sodium or potassium citrate, the extinction coefficient of the resulting yellow solution may be determined in a step photometer.[187]

Hoffman and Osgood [184] have used an aqueous solution of ammonium thiocyanate to stabilize the color of the triple acetate against temperature change. Sumuleanu and Bottezatu [125] recommend dissolving the sodium zinc uranyl acetate precipitate in water and adding pyrocatechol and sodium hydroxide for the color comparison. They used permanent standards prepared from Bismarck brown. Sodium salicylate has been used to develop the color of aqueous solutions of the triple acetate.[49,153] Sulfosalicylic acid has also been used to develop the color with uranium in the triple acetate precipitate.[154] This color is stable against time and temperature. Ishibishi and Kishi [62] have used thorium B as a radio active indicator of the uranium content of sodium magnesium uranyl acetate. Goto [155] has studied the fluorescence of sodium zinc uranyl acetate as a basis for the sodium determination. Fredericq [228] determined sodium after precipitating with magnesium uranyl acetate by measuring the violet color given by treating the dissolved precipitate with alizarin.

Other uranyl acetate reagents. A number of uranyl acetate reagents containing bivalent metals other than zinc and cadmium have been proposed for the sodium precipitation. These reagents have been of value only in qualitative analysis. Among the metal acetates that have been used are cadmium [176,177,183]; nickel; [98,176-178,180,183] manganese; [176,178,181-184] cobalt; [176,178-180,188] copper and iron; [175-178,183,209] and lead.[58]

BASIC ACETATE SEPARATIONS

A number of important separations are based upon the fact that ferric, aluminum and titanium acetates are hydrolyzed in hot dilute solutions much more readily than the acetates of the bivalent metals. Upon the hydrolysis of ferric acetate, acetic acid is formed according to the equation

$$Fe(C_2H_3O_2)_3 + H_2O \rightleftarrows 2HC_2H_3O_2 + Fe(OH)_2 \cdot C_2H_3O_2$$

and this tends to reverse the reaction due to the solvent effect of the hydrogen ion upon the basic ferric acetate. The concentration of the hydrogen ions may, however, be reduced by the addition of sodium acetate to insure the reaction running to completion. Among the metals from which iron, aluminum and titanium may be separated are manganese, nickel, cobalt and zinc. Ferric iron may be quantitatively precipitated by adjusting the pH of the solution to 5-6 with acetic acid and sodium acetate and heating. The following procedure may be used for the separation of iron, aluminum and titanium from manganese, cobalt, nickel and zinc:[211-214]

Procedure. To a slightly acid solution containing the chlorides of the metals, add a solution of sodium carbonate until a slight permanent opalescence appears. Add a few drops of dilute hydrochloric acid to redissolve the precipitate. In a large round-bottomed flask prepare a dilute solution of sodium or ammonium acetate which contains for each 0.1-0.2 g. of iron or aluminum, 1.5-2 g. of the acetate and 300 ml. of water. Heat the acetate solution to boiling and remove the burner. Then add the solution to be analyzed and replace the burner and boil the mixture for 1 minute. Discontinue the heating and allow the precipitate to settle. Filter while hot and wash 3 times by decantation with boiling water containing sodium or ammonium acetate. Transfer the greater part of the precipitate to a porcelain dish and dissolve the remainder from the paper by alternately treating with hot 3 N hydrochloric acid and hot water. Evaporate the resulting solution almost to dryness on a water-bath and repeat the precipitation as described above. Then dissolve the filtered and washed precipitate in hydrochloric acid and separate the iron and aluminum according to the usual methods. Manganese, nickel, cobalt and zinc may be determined in the combined filtrates.

The above method is especially suited for the separation of iron and titanium from the other metals, but the method is usually less satisfactroy with aluminum. Some manganese may precipitate during the basic acetate precipitation, and so it is necessary to dissolve the precipitate and carry out the precipitation a second time.

Iron may be separated from manganese in the absence of other metals by the following method, which requires but a single precipitation.[215-217]

Procedure. To the acid solution containing not more than 0.3 g. of iron, add 0.35 g. of potassium chloride for each 0.1 g. of iron. Evaporate to dryness on a water-bath and break up the residue with the aid of a stirring rod. Heat for an additional 5 or 10 minutes and dissolve the residue in 10-20 ml. of water. Now add 1.5 g. of sodium acetate for each 0.1 g. of iron present, and dilute with boiling water to a volume of 200 ml. for each 0.1 g. of iron present. Heat to boiling with stirring and remove the burner. Allow the precipitate to settle, decant the solution through a filter, and wash the precipitate with hot water. Dissolve the precipitate in a minimum quantity of hydrochloric acid and precipitate iron with ammonium hydroxide. Filter, dry, and ignite to Fe_2O_3.

The following method for separating iron and manganese has been proposed by Mittasch:[218]

Procedure. Neutralize the slightly acid solution, containing not more than 0.3 g. of iron and having a volume not greater than 100 ml., by adding a 20 per cent ammonium carbonate solution from a buret while stirring constantly. When a precipitate is formed which dissolves only very slowly with stirring, complete the neutralization by adding a more dilute solution of ammonium carbonate prepared by diluting 50 ml. of the more concentrated solution to 1 liter. Neutralization is indicated by the formation of a slight precipitate which does not dissolve after 1 or 2 minutes of stirring. When this occurs add 3 ml. of 2 N acetic acid and stir until the precipitate is dissolved. Dilute the solution with 400 ml. of hot water and heat until the mixture just begins to boil. Then add 20 ml. of a solution prepared by dissolving 60 g. of ammonium acetate ($NH_4C_2H_3O_2 \cdot HC_2H_3O_2$) in 1 liter of water and boil for 1 minute. Filter immediately and wash free of chlorides with hot water. Add a little hydrochloric acid to the beaker in which the precipitation was carried out to dissolve the small quantity of precipitate remaining in the vessel, and precipitate the iron from this solution with ammonium hydroxide. Filter the ferric hydroxide through a separate filter. Ignite both precipitates and filters and weigh as Fe_2O_3.

Separation of iron and nickel. Hanus and Vorisek[196] have studied the basic acetate method for separating iron and nickel.

Separation of chromium. Chromium reacts with acetic acid and acetates to form complex salts derived from extremely stable polynuclear compounds. These are formed when solutions of chromic salts are boiled with alkali acetates. Solutions prepared in this manner remain perfectly clear and yield no precipitate even on the addition of an alkali phosphate.[229] In this property chromium differs from ferric iron and aluminum, which on boiling with acetates yield precipitates of hydrated oxides or basic salts. Unfortunately, however, precipitation of ferric and aluminum salts by alkali acetates is partially prevented if chromic salts are present,[230] and chromium is present in the precipitates formed. For this reason the acetate complexes do not appear suitable for the separation of iron and aluminum from chromium, but they may be very useful for masking chromium in various analytical reactions.[231,232]

Separation of zirconium and titanium from iron. In the presence of sodium acetate, titanium and zirconium may be completely separated from iron if the latter is kept in the ferrous state.[219]

Separation of aluminum and iron from titanium. One of the best methods for the separation of aluminum from titanium is that proposed by Gooch.[220] This consists of boiling a solution of the two elements to which have been added acetic acid and an alkali acetate. In this way all titanium and none of the aluminum is precipitated. The separation must be repeated if the amount of aluminum is large. Since in most cases both aluminum and iron are present, the following procedure is described for the separation of aluminum and iron from titanium:

Procedure. Fuse the mixture of oxides with 15-20 times as much potassium pyrosulfate and dissolve the cold mass in cold 2.5 per cent sulfuric acid. Add 3 times as much tartaric acid as the weight of the oxides initially used. Saturate the solution with hydrogen sulfide, and then add ammonium hydroxide until slightly alkaline. Filter off the iron sulfide and acidify the filtrate with sulfuric acid. Heat to boiling, filter, and boil the filtrate to expel the last traces of hydrogen sulfide. Add 2.5 times as much potassium permanganate as tartaric acid used, and then add sulfurous acid until the precipitated manganese dioxide is redissolved. Add a slight excess of ammonia and 7-10 ml. of glacial acetic acid for each 100 ml. of solution. Boil for 1 minute, allow the precipitate to settle and decant through a filter. Finally transfer the precipitate to the filter and wash, first with 7 per cent acetic acid, and finally with a little hot water. Ignite and weigh as TiO_2.

Fuse the impure TiO_2 with 3 times as much sodium carbonate and treat the melt with cold water. Filter through a small filter and ignite the residue in a platinum crucible. Again fuse with a little sodium carbonate. Allow to cool, and dissolve in 200 ml. of 0.1 N sulfuric acid. Add 5 g. of sodium acetate and 20 ml. of glacial acetic acid and boil for 1 minute. Allow to stand, filter, and wash, first with 7 per cent acetic acid and then with water. Dry, ignite and weigh.

Since the precipitate may contain aluminum, it should again be fused with sodium carbonate, treated with sulfuric acid and precipitated as described above. This procedure should be repeated until a constant weight is obtained.

Separation of manganese and cobalt. Funk [221] has based a method for the separation of manganese from cobalt upon the fact that manganese sulfide is soluble in acetic and formic acids.

Detection of beryllium. Unlike other metals, beryllium forms a volatile basic acetate. To prepare this compound dissolve beryllium hydroxide in acetic acid, evaporate to a thick gummy mass, then dissolve in glacial acetic acid and boil off the excess acid. On cooling the basic acetate separates as octahedral crystals.[222,223]

Beryllium may be separated from aluminum by a procedure based upon the fact that $BeO \cdot 3Be(C_2H_3O_2)_2$ is soluble in chloroform.[224] The separation is effected by dissolving the freshly precipitated hydroxides of aluminum and beryllium in glacial acetic acid, evaporating with a little water, and extracting the residue with chloroform.

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ADIPIC ACID

$C_6H_{10}O_4$ Mol. Wt. 146.14 Beil. Ref. II, 649.

$$HO_2C—CH_2—CH_2—CH_2—CH_2—CO_2H$$

Use: Standardization of solutions of bases and potassium permanganate.

Adipic acid is a white, crystalline powder. It melts at 152° C. and boils at 265° C. (100 mm.). The acid is soluble in 70 parts of water, slightly soluble in ether, but is readily soluble in alcohol.

Preparation: Place 2100 g. of 50 per cent nitric acid (d. 1.32) in a 5-liter flask fitted with a separatory funnel and a thermometer. Heat nearly to boiling and add about 1 g. of ammonium vanadate, and then add slowly through the separatory funnel 500 g. of cyclohexanol with stirring. Add 1-2 ml. of cyclohexanol at first, and stir until the reaction is started. Then immerse the flask in an ice-bath and cool until the temperature is 55-60° C., and then add the remainder of the cyclohexanol as rapidly as possible with agitation, keeping the temperature of the mixture between 55-60° C. Toward the end of the oxidation, remove the ice-bath and warm the mixture. Allow to stand about 1 hour with stirring. Cool to 0° C., filter with suction, wash with 500 ml. ice water, and dry in air.[1]

Titrimetric standard: Adipic acid has been recommended as an alkalimetric standard by Van Voorst [2] and Kolthoff.[6] The compound is easy to prepare, and the commercial product is easily purified by recrystallizing two times from five times its weight of distilled water and then drying at 130° C. The pure acid melts at 152.05° C., its density is 1.366, and its equivalent weight is 73.07.

According to Schoorl,[3] however, oxalic acid is the better standard, and Jorissen[4] prefers oxalic acid for standardizing potassium permanganate solutions. Meyling[5] has also studied adipic acid and feels that its use is to be encouraged.

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BENZOIC ACID

Synonym: Benzenecarboxylic acid

$C_7H_6O_2$ Mol. Wt. 122.12 Beil. Ref. IX, 92.

$C_6H_5CO_2H$

Uses: Alkalimetric standard. Detection of thallium.

Detection of aluminum, chromium and iron.

Determination of aluminum, calcium hydroxide, chromium, copper, iron, thorium and vanadium.

Benzoic acid consists of colorless or white lustrous needles or leaflets. It begins to sublime at 100° C. and melts at 120-21° C. It boils at 249° C. and is volatile with steam. A saturated solution has a pH of 2.8. One gram of the solid dissolves in 275 ml. of cold water and 18 ml. of boiling water. One gram dissolves in 2.3 ml. of cold alcohol, 4.5 ml. of chloroform, 3 ml. of ether, 3 ml. of acetone, 10 ml. of benzene, 30 ml. of carbon tetrachloride and 30 ml. of carbon disulfide.

Separation of aluminum, iron and chromium. Kolthoff, Stenger and Moskovitz[1] have used benzoic acid for the separation of aluminum, chromium and iron from other ions of the third analytical group and the alkaline earth metals. The reagent is said to be more satisfactory than ammonium hydroxide for this purpose, since there is less co-precipitation. The separation is also claimed to be more satisfactory than the basic acetate method.

Procedure. To 100 ml. of a solution containing 0.05-0.2 g. of the ions to be precipitated, add ammonium hydroxide until the precipitate which first forms redissolves very slowly on stirring. Then add 1 ml. of acetic acid and sufficient ammonium chloride to make the total content at least 1 g. Then add slowly with stirring 20 ml. of 10 per cent ammonium benzoate for each 65 mg. of aluminum, 125 mg. of iron or 125 mg. of chromium. Heat just to boiling and keep the solution at this temperature for 5-20 minutes depending upon whether chromium is present or absent. Filter, and wash the precipitate with hot 1 per cent ammonium benzoate solution containing 2 per cent acetic acid. For accurate work the precipitate should be dissolved in acid and reprecipitated according to the above procedure.

The precipitate, which may contain aluminum, chromium and iron, is treated as follows: add 1 N sodium hydroxide and hydrogen peroxide, and boil to remove the excess peroxide. Ferric oxide remains insoluble, while chromium and aluminum dissolve. Filter, and determine iron in the residue by any of the usual methods. Acidify the filtrate and precipitate aluminum by the benzoate method. Filter and determine aluminum in the residue by first dissolving, and then precipitating from an ammoniacal tartrate solution with 8-hydroxyquinoline. Chromium is determined in the filtrate by a titration procedure.

The metals which are precipitated by ammonium benzoate in acetic acid solution according to the above procedure are given in Table 3.

TABLE 3.—PRECIPITATION OF METALS WITH AMMONIUM BENZOATE IN ACETIC ACID SOLUTION

Quantitative Precipitation		Partial Precipitation	
Ion	Color of Precipitate	Ion	Color of Precipitate
Aluminum	white	Uranium	yellow
Chromium	gray-green	Beryllium	white
Iron	orange-tan	Titanium (ous)*	brown
Titanium (ic)	white	Lead	white
Zirconium	white	Copper	light blue
Thorium	white	Tin (ous)*	white
Cerium (ic)	yellow		
Bismuth	white		
Tin(ic)	white		

* Oxidized under experimental conditions to yield precipitates of oxidized forms.

The following metals are not precipitated by ammonium benzoate under the conditions outlined in the above procedure: vanadium, cobalt, nickel, manganese, zinc, calcium, strontium, barium, magnesium, potassium, sodium, ammonium, lithium, iron (ous), cadmium, mercury (ic), cerium (ous). Ferrous and cerous salts are oxidized under the conditions outlined in the determination to yield precipitates of the oxidized form.

The benzoate separation has been studied by Lehrman and Kramer,[2] who have found that it is excellent for separating ferric iron, chromium and aluminum from various bivalent metal ions. Before testing for the latter, however, they recommend that the acid filtrate be evaporated until most of the benzoic acid has crystallized and has been removed by filtration.

In a critical study of the method of Kolthoff, Stenger and Moskovitz,[1] Paris[3] has arrived at the following conclusions: (a) Either iron or aluminum may be determined accurately by precipitation with ammonium benzoate; (b) the separation of iron and aluminum from manganese, cobalt and nickel is fairly satisfactory when smaller quantities of bivalent ions than of trivalent ions are present; and (c) the separation of iron and aluminum from zinc is less satisfactory.

A method which makes use of a benzoic acid-ammonium benzoate buffer for the precipitation of iron, aluminum and chromium as a complex benzoate at pH 3.8 has been used successfully in a scheme of qualitative analysis by Tomsicek and Carney.[4] This procedure affords a number of advantages over other methods which have been used: (a) a complete separation of the hydrous oxides from the bivalent ions of the same group is readily effected; (b) there is little danger of precipitation of the hydroxide or oxy-hydroxide of manganese; and, (c) the precipitates are readily coagulated and may be rapidly filtered from the warm solution.

Determination of chromium and aluminum. The following procedure is used for the separation of chromium and vanadium in titanium magnitite ores.[5]

Procedure. Mix 1 g. of the dry ore with 8 g. of sodium peroxide and ignite for 15 minutes. Dissolve the melt in water and boil. Filter, and to the filtrate (100-150 ml.) add dropwise 25 per cent nitric acid. Filter any precipitate of silica and aluminum hydroxide. Filter and make the filtrate neutral to litmus with 10 per cent nitric acid and add 2 ml. of acetic acid. Then precipitate chromium and vanadium with lead acetate and boil for 2 minutes. Filter and wash the precipitate with warm water and dissolve on the filter with hot 10 per cent nitric acid. Add 10 ml. of 50 per cent sulfuric acid, evaporate to fumes and dilute with 50 ml. of water. If the precipitate is yellow add 3-4 ml. of nitric acid and again evaporate to fumes. Filter to remove lead sulfate and wash with 50 per cent alcohol and evaporate the filtrate to about 80 ml. Treat the solution, which contains chromium and vanadium, with 25 per cent ammonium hydroxide to the first appearance of a permanent turbidity, and then add 2 ml. of acetic acid and 1 g. of ammonium chloride. Add quickly 15-20 ml. of 10 per cent ammonium benzoate and boil gently for 20 minutes. Wash the precipitate 10 times with hot water containing 2 ml. of acetic acid and 2 ml. of 10 per cent ammonium benzoate solution in 500 ml. Evaporate the filtrate to 50-60 ml., and filter again if more precipitate forms. Dry the filter and precipitate, incinerate, and ignite at 900-1000° C. for 20 minutes. Weigh as Cr_2O_3.

8-Hydroxyquinoline has been used for the determination of aluminum in magnesium alloys low in manganese, zinc and other interfering elements, but since most commercial alloys contain one or more of these metals, preliminary separations are necessary for an accurate determination. The precipitation of aluminum as the hydroxyquinolate from ammoniacal tartrate solutions or from solutions containing an acetic acid-acetate buffer requires a preliminary removal of magnesium. The addition of ammonium benzoate to an acetic acid solution of these metals has been shown to give a fairly complete separation of aluminum from most of the bivalent elements in one step.[1] The benzoate precipitate is readily soluble in a warm ammoniacal tartrate solution, from which aluminum can be precipitated with 8-hydroxyquinoline. This principle has been employed by Stenger, Kramer and Beshgetoor[6] for the determination of aluminum in magnesium alloys.

Reagents. *Ammonium benzoate solution:* Dissolve 100 g. of pure ammonium benzoate in a liter of warm water and add 1 mg. of thymol as a preservative.

Benzoate wash solution: Add 900 ml. of warm water and 20 ml. of glacial acetic acid to 100 ml. of the ammonium benzoate solution.

8-Hydroxyquinoline solution: Dissolve 50 g. of 8-hydroxyquinoline in 1 liter of water containing 120 ml. of glacial acetic acid. Filter if necessary and store in a dark bottle.

Ammoniacal tartrate solution: Dissolve 30 g. of ammonium tartrate in a liter of water containing 120 ml. of concentrated ammonium hydroxide.

Procedure. To a weighed sample of the alloy containing 0.2-0.5 g. of aluminum, add 25 ml. of water and dissolve by adding in small portions 10 ml. of hydrochloric acid for each gram of sample. Cool the resulting solution to room temperature and dilute to 500 ml. in a volumetric flask. Prevent any undissolved silica from settling, and pipet a 50-ml. aliquot into a 400-ml. beaker and add 50 ml. of water.

Add 1:1 ammonium hydroxide dropwise and with stirring until the precipitate which forms upon the addition of each drop finally dissolves very slowly. At this point all free hydrochloric acid is neutralized while aluminum hydroxide is not permanently precipitated. Then add 1 ml. of glacial acetic acid, 1 g. of ammonium chloride and 20 ml. of ammonium benzoate solution. Heat to boiling with stirring and boil gently for 5 minutes. Filter with suction on a previously weighed glass crucible of the Gooch type, which is fitted with a fritted disc of fine porosity. Wash 8-10 times with the hot benzoate wash solution. It is not necessary to transfer all the precipitate to the crucible. Return the precipitate to the beaker in which the precipitation was carried out, transferring most of it with the aid of a stirring rod and washing in the remainder with water. Dissolve the small part remaining in the crucible by washing 5 times with 10-ml. portions of the hot ammoniacal tartrate solution, and combine these washings with the precipitate in the beaker. Heat to 70-90° C. and add 25 ml. of the 8-hydroxyquinoline solution. Heat for 30 minutes without boiling and filter through the same crucible which was used previously to collect the benzoate precipitate. Wash 8 times with water, this time transferring all of the precipitate to the crucible. Dry for 1.5-2 hours at 120-130° C. Cool, and weigh as $Al(C_9H_6ON)_3$.

The aluminum content is calculated from the following equation:

$$\% \text{ Al} = \frac{\text{weight of precipitate} \times 0.05873 \times 100}{\text{grams of sample in aliquot}}$$

The results obtained using this method in the presence of various ions is given in Table 4.

TABLE 4.—DETERMINATION OF ALUMINUM BY THE BENZOATE-8-HYDROXYQUINOLINE METHOD

Aluminum Taken mg.	Additions mg.	Aluminum Found mg.	Error Per Cent
25.00	None	24.92	—0.32
25.00	None	24.98	—0.08
50.00	None	50.08	+0.16
10.00	500 Mg.	9.99	—0.10
25.00	500 Mg.	25.05	+0.20
50.00	500 Mg.	49.86	—0.28
25.00	25 Zn	25.09	+0.36
10.00	500 Mg, 10 Zn	9.96	—0.40
10.00	500 Mg, 10 Zn	10.01	+0.10
25.00	500 Mg, 10 Zn	24.96	—0.16
25.00	500 Mg, 10 Zn	25.04	+0.16
10.00	500 Mg, 25 Zn	10.02	+0.20
10.00	500 Mg, 25 Zn	10.06	+0.60
25.00	500 Mg, 25 Zn	24.93	—0.28
25.00	500 Mg, 25 Zn	25.01	+0.04
25.00	500 Mg, 25 Mn	24.93	—0.28
25.00	500 Mg, 25 Mn, 25 Zn	24.96	—0.16
25.00	500 Mg, 2 Mn, 15 Zn	24.92	—0.32
50.00	500 Mg, 1 Mn, 10 Zn	49.92	—0.16
25.00	500 Mg, 25 Cd	24.88	—0.48
50.00	500 Mg, 10 Cu	50.36	+0.72
50.00	25 Cu	50.60	+1.2
25.00	500 Mg, 25 Sn	25.25	+1.0
25.00	500 Mg, 25 Sn	25.30	+1.2
25.00	500 Mg, 1 Fe	25.19	+0.76
25.00	500 Mg, 1 Fe	25.24	+0.96

Pollack and Pellows[22] have determined aluminum in spelter by first separating as the benzoate, then precipitating with 8-hydroxyquinoline, and finally titrating with potassium bromate-potassium bromide.

Determination of vanadium. Ammonium benzoate precipitates tetravalent vanadium quantitatively from solutions of its ores and alloys. The precipitation may be carried out without previously removing magnesium, aluminum, copper, molybdenum, tungsten and titanium. Iron and chromium, however, must be absent. The following procedure is recommended by Shemyakin:[7,8]

Procedure. To 25 ml. of a solution containing 0.1-0.15 g. of V_2O_5 add 10 ml. of 2 N hydrochloric acid and heat to boiling. Add dropwise and with stirring a saturated solution of ammonium sulfite until the mixture is completely decolorized. Then add a hot solution of ammonium benzoate (saturated when cold) to precipitate vanadium. At least 1 g. of ammonium benzoate is needed for each 0.1 g. of V_2O_5. Boil the mixture for 2-3 minutes and allow to stand for 3-4 hours. Filter the precipitate and wash with a cold saturated solution of benzoic acid. Dry at 100-120° C. and ignite for 15 minutes to V_2O_5.

The results obtained by this method are said to be accurate to within 0.001 per cent, and are not affected by the presence of magnesium, aluminum, copper, molybdenum, tungsten or titanium. Iron and chromium must first be separated.

Determination of copper. When ammonium benzoate and hexamethylenetetramine are added to a solution of cupric ions in hot dilute nitric acid, a light blue complex salt of hexamethylenetetramine benzoate is formed. This corresponds to the formula $Cu_3(C_6H_5CO_2)_6 \cdot C_6H_{12}N_4$. This precipitate may be dried and weighed or ignited to CuO:[9]

Procedure. To 50-100 ml. of a solution containing up to 0.1 g. of copper, add a solution of 0.5-1 g. of ammonium benzoate and an equal weight of hexamethylenetetramine dissolved in about 20 ml. of water. Stir, filter, and wash with a solution containing 3 g. of ammonium benzoate and 0.3 g. of hexamethylenetetramine per liter. Finally wash successively with water, alcohol and ether and then dry in vacuum and weigh.

The factor for copper is 0.1804. If the quantity of precipitate is large, ignite to CuO.

A blue precipitate of $[CuPy_2](C_6H_5CO_2)_2$ is formed when sodium benzoate is added to a solution of a copper salt containing pyridine. The formation of this compound has been used by Dick and Radulescu[10] for the determination of copper and for its separation from lead.

Procedure. To 40-50 ml. of a copper solution add pyridine in slight excess until an azure blue color is obtained. For 0.1 g. of copper, 20-25 drops of pyridine is sufficient. Then add about 3 g. of ammonium benzoate dissolved in 20-25 ml. of water to precipitate the complex copper compound. Filter and wash with a solution of 1.5 g. of ammonium benzoate and 1 ml. of pyridine in 100 ml. of water. Dry, ignite and weigh as CuO.

Copper may be precipitated in the presence of lead by a similar procedure. For this separation addition of 2-3 g. of ammonium acetate is necessary. After filtering off the copper compound, lead may be determined in the filtrate as lead chromate.

Determination of thorium. Neish[11] and Kolb and Ahrle[12] have used benzoic acid for the precipitation of thorium. According to Neish[11] benzoic acid precipitates thorium quantitatively from aqueous solutions while cerium, lanthanum, praseodymium and neodymium are not precipitated. This reaction is not particularly useful, however, due to the slight solubility of benzoic acid in water.

Determination of calcium hydroxide. Smith and Hendricks [13] have used benzoic acid for the determination of free calcium hydroxide in commercial calcium arsenate. To make this determination proceed as follows:

Procedure. Treat 1 g. of the sample which will pass a 100-mesh sieve with 50 ml. of 0.1 N benzoic acid solution in 93 per cent alcohol. Shake for 5-6 minutes in a stoppered flask and titrate the excess benzoic acid with 0.1 N sodium hydroxide in 93 per cent alcohol. Use phenolphthalein as the indicator. Benzoic acid appears to react with calcium hydroxide but not with calcium carbonate or calcium arsenate. It is necessary to agitate the solution violently during the back titration. Best results are obtained if just before the end-point, the mixture is filtered through paper, the latter washed 1-2 times with alcohol, and the filtrate titrated with the sodium hydroxide solution.

The usual methods of determination using aqueous solutions are unsatisfactory because of the hydrolysis of calcium arsenate.

Detection of thallium. Deniges [14] has used a 5 per cent sodium benzoate solution as a microchemical reagent for the detection of thallium. Thallium is detected by means of a characteristic microcrystalline precipitate.

Alkalimetric standard. The use of benzoic acid as an alkalimetric standard has been suggested by Wagner,[15] and it has been recommended by Phelps and Weed [16] and especially by Morey.[17,18] Morey [17,18] states that this reagent possesses the advantage of a high molecular weight which permits the use of large samples and thus reduces the error caused by weighing. Further, the purity, stability and lack of hygroscopicity also make its use desirable.

Commercial benzoic acid may be purified by recrystallizing twice from alcohol, once from water and then fractionally subliming in vacuum. The resulting product is very voluminous and should be fused in a covered glass or platinum vessel in an air-bath. The temperature during the fusion must not rise above 140° C. and preferably not above 130° C. The fused product should be perfectly colorless. Any decomposition which can be detected chemically imparts a distinct yellow color to the product.[19] After the compound is melted, it is poured immediately into a test tube and allowed to solidify. The stick of benzoic acid thus obtained is broken up into small pieces and preserved in a glass-stoppered bottle. The sample will keep indefinitely and may be used without preliminary drying since surface condensation is very slight and may be neglected. Although the acid is not hygroscopic, after long standing, especially in a container that has been opened from time to time, a little moisture may be absorbed and may cause changes approximating 0.1 per cent.

The equivalent weight of benzoic acid is 122.12. The normality of the alkali solution is calculated from the following equation:

$$C_6H_5CO_2H + NaOH \rightarrow C_6H_5CO_2Na + H_2O$$

The following method for standardizing solutions of bases is carried out according to the procedure described by Morey:[18]

Procedure. Weigh 1.5-2.0 g. of the acid into a 300-ml. flask and add 40 ml. of alcohol. Stopper the flask and allow to stand until the acid is dissolved. Then add 3 drops of phenolphthalein indicator and titrate directly with 0.1 N alkali hydroxide or dilute to 100 ml. and titrate with 0.5 N alkali hydroxide. Make a determination using a blank with the alcohol and the same volume of water as present at end of the titration, and make a corresponding deduction in all titrations for the volume of base required to react with the indicator.

More recently Lipin and co-workers [20] have examined the use of benzoic acid as an alkalimetric standard, and report that results are entirely satisfactory.

MacInnes and Cowperthwaite [21] have devised a differential electrometric method of titration that has been adapted to the use of hydrogen electrodes, and the method has been applied to precise acidimetry. Benzoic acid has been used with results that are accurate to 0.01 per cent.

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BUTYRIC ACID

$C_4H_8O_2$ Mol. Wt. 88.10 **Beil. Ref. II, 264.**

$$CH_3—CH_2—CH_2—CO_2H$$

Use: Determination of copper.

Butyric acid is a clear, oily liquid having an extremely unpleasant odor. Its sp. gr. is 0.959 and it boils at 162° C. It is miscible with water, alcohol and ether.

Determination of copper. Interference by iron with the electrolytic determination of copper can be eliminated by the addition of a little butyric acid to the electrolytic bath.[1]

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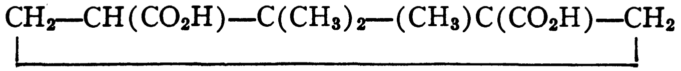
CAMPHORIC ACID

Synonym: d-Camphoric acid

$C_{10}H_{16}O_4$ Mol. Wt. 200.23 Beil. Ref. IX, 745.



$$\underbrace{CH_2—CH(CO_2H)—C(CH_3)_2—(CH_3)C(CO_2H)—CH_2}$$

Uses: Determination of gallium and water. Separation of gallium from thallium and iron.

Camphoric acid consists of colorless or white, odorless crystals. The melting point is 186-188° C. and the sp. gr. is 1.186. One gram of the reagent dissolves in 125 ml. of cold water, 10 ml. of boiling water, 1 ml. of alcohol, and 20 ml. of glycerol. It is also soluble in chloroform and ether.

Preparation: Dissolve 152 g. of d-camphor in toluene and heat 5-8 hours with 23 g. of sodium until all the sodium has dissolved. Saturate the resulting hot solution with carbon dioxide, then treat with water and allow the mixture to stand 4 hours. Filter, and acidify the filtrate, and purify the product by crystallization from hot (not boiling) water.[1]

Separation and determination of gallium. Gallium is precipitated from a solution of its chloride or nitrate by the addition of camphoric acid. The precipitate may be ignited and weighed as Ga_2O_3. As precipitant, use camphoric acid, a solution of 25 g. of reagent in 250 ml. of alcohol, or a solution of 10 g. of reagent in 100 ml. of acetone.[2] Precipitation is carried out with sodium camphorate in a solution which has been made barely acid with acetic acid.[3]

According to Ato,[4] gallium can be separated from thallium by first reducing the latter to the monovalent state, and then precipitating gallium with camphoric acid. To separate gallium from iron, reduce the iron to the ferrous state and precipitate gallium with camphoric acid.

In a critical study of the various methods for determining gallium, Wenger and Duckert[5] report that camphoric acid is not a sufficiently sensitive reagent to give satisfactory results. Morin is better.

Determination of water in acetic acid. Toennies and Elliott[6] have proposed an interesting method for determining water in acetic acid. The water is allowed to react with a known quantity of acetic anhydride, and the excess acetic anhydride determined by the decrease in the optical rotation caused by its reaction with d-camphoric acid. d-Camphoric anhydride is formed. Both reactions are catalyzed strongly by low concentrations of strong acids. By this procedure, 0.1-0.6 per cent water can be determined in acetic acid with an accuracy of 0.008 per cent.

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CINNAMIC ACID

Synonym: β-Phenylacrylic acid

$C_9H_8O_2$ Mol. Wt. 148.15 Beil. Ref. IX, 572.

$$C_6H_5—CH=CH—CO_2H$$

Uses: Determination of uranium and vanadium. Separation of thorium.

Cinnamic acid is a white crystalline solid. It possesses a slight cinnamon-like odor. It melts at 133° C. and boils at 300° C. One gram of the solid dissolves in about 2 liters of water at 25° C., although it is more soluble in hot water. One gram of the solid also dissolves in 6 ml. of alcohol, 5 ml. of methyl alcohol or 12 ml. of chloroform. The compound dissolves readily in benzene, ether, acetone, glacial acetic acid and carbon disulfide.

Preparation. Place 12 g. of freshly fused and pulverized potassium acetate in a dry 200-ml. flask, and add 28 ml. of acetic anhydride and 20 ml. of freshly distilled benzaldehyde. Fit the flask with a reflux condenser, and heat the mixture in an oil bath at 155-160° C. for one hour. Then increase the temperature to 160-170° C. and heat at this temperature for 3-3.5 hours.

While still hot, pour the contents of the flask into a 2-liter round-bottom flask, and rinse the flask in which the reaction was carried out with two 100-ml. portions of boiling water. Add 300-350 ml. of water, and steam distill until all unchanged benzaldehyde has been removed.

Dilute the residue in the flask to 1200 ml. with water, and heat to boiling. Cool slightly, and add 3-4 g. of decolorizing charcoal, and then boil the solution gently for 5-10 minutes. Filter the hot solution, and heat the filtrate to boiling.

Add 12-14 ml. of concentrated hydrochloric acid, and allow the solution to cool with stirring. Allow to stand for a time, and filter with suction. Wash the crystals with several small portions of water, and dry.[1]

Determination of vanadium. Ammonium cinnamate may be substituted for ammonium benzoate as a precipitant for vanadium.[2] The following procedure is reported to give good results:

Procedure. Acidify a hot solution containing about 0.13 g. of V_2O_5 in 25 ml. of water with 10 ml. of 2 N hydrochloric acid and heat to boiling. Reduce the vanadium by adding 10 ml. of a saturated solution of ammonium sulfite drop by drop to the appearance of a light blue color. Then add a hot 8 per cent solution of ammonium cinnamate, boil for 2 or 3 minutes, and allow the mixture to stand for 3 or 4 hours. Filter and wash the precipitate with a saturated solution of cinnamic acid. Dry at 100-110° C. and ignite and weigh as V_2O_5.

Kolb and Ahrle[3] have found that cinnamic acid can be used in place of benzoic, salicylic or *m*-nitrobenzoic acid for the precipitation of thorium from neutral solutions of its salts.

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FORMIC ACID

CH_2O_2 Mol. Wt. 46.03 Beil. Ref. II, 8.

$H—CO_2H$

Use: Detection of cerium, rhenium, silver and tungsten.

Determination of arsenic, bismuth, cobalt, copper, gold, indium, iron, lead, manganese, mercury, molybdenum, nickel, nitric acid, palladium, platinum, silver, tungsten, and zinc.

Formic acid is a colorless liquid which has a very pungent odor and an irritating effect on the skin. The acid boils at 100.5° C. and has a sp. gr. of 1.220. It is miscible with water, alcohol, ether and glycerol. It is a powerful reducing agent. The commercial product usually contains only 85-90 per cent formic acid.

Separation and determination of bismuth. Benkert and Smith[1] state that bismuth may be completely separated from lead by boiling a nearly neutral solution of their salts with an excess of a solution of sodium formate containing a little formic acid. The precipitate so formed contains a little lead, but this may be removed by redissolving in nitric acid and precipitating a second time. The precipitate of basic bismuth formate is then dissolved in dilute nitric acid and precipitated with ammonium carbonate. Ostroumov[2,3] has reported that the separation of bismuth by this method does not give good results. Kallman,[4] however, has found that the method of Benkert and Smith[1] has advantages over other separation procedures that have been proposed, but that there are certain objections to its general use.

A new procedure proposed by Kallman [4] is claimed to be superior to existing methods. This method is adaptable both to the quantitative separation and determination of bismuth and lead, and for the quantitative separation of small quantities of bismuth from large amounts of lead.

Reagent. *Ammonium formate solution:* Dilute 300 ml. of 90 per cent formic acid with 100 ml. of water and neutralize with 12 N ammonium hydroxide using litmus paper as the indicator. About 650 ml. of ammonium hydroxide are required for this purpose.

Procedure. To the warm nitric acid solution of bismuth and lead, containing not more than 0.4 g. of bismuth, add 4 N ammonium hydroxide dropwise until a permanent precipitate is formed. Then add 8 N nitric acid dropwise until the precipitate just dissolves. Neutralize the excess nitric acid carefully with 5 per cent ammonium carbonate until further addition would cause the precipitation of basic bismuth carbonate. The solution should be clear at this point.

Heat the mixture to boiling and continue to boil for 5 minutes. Then add 7-8 ml. of the ammonium formate solution and again heat to boiling. Allow to stand on a hot plate or water-bath for 15 minutes, or for about 2 hours if only 1 mg. or less of bismuth is present. Filter through a No. 42 Whatman or similar grade paper and wash the precipitate 5 times with hot water. Wash the precipitate back into the original beaker and dissolve in 5-6 ml. of 8 N nitric acid.

Again precipitate with ammonium formate as described above and filter through the original paper and into the original filtrate. Wash the precipitate 8 times with hot water. Save the filtrates for the determination of lead. Wash the precipitate once with alcohol, and then ignite cautiously in a weighed crucible. As the paper is burned off, cool and moisten the precipitate with 8 N nitric acid. Dry on a hot plate and ignite cautiously to Bi_2O_3.

If less than 0.7 mg. of bismuth is present, dissolve the bismuth formate precipitate in hot 1:3 sulfuric acid and transfer the solution, or a suitable aliquot, to a 50-ml. Nessler tube. Add 2-3 drops of dilute sulfur dioxide solution and about 2 g. of potassium iodide and dilute to 50 ml. Compare in a colorimeter with another tube containing the same amounts of sulfurous acid and potassium iodide and the same volume of solution. To the comparison tube, add a standard bismuth sulfate solution containing 0.1 g. of bismuth per liter until the colors of the two solutions match.

Lead may be determined in the filtrate as follows: Add 30 ml. of nitric acid to the combined filtrates from the bismuth formate separation and evaporate to 20-30 ml. or until heavy white fumes appear. Then add 5 ml. of 16 N nitric acid and 30 ml. of 33 per cent ammonium acetate solution. Dilute to 250 ml., heat to boiling, and add an excess of hot potassium dichromate solution. Boil for 2-3 minutes until the precipitate turns orange and filter on a weighed Gooch crucible. Wash with hot water, dry at 105° C. and weigh as lead chromate. The factor for lead is 0.6411.

Extreme care must be used in the neutralization of the bismuth and lead nitrate solution when bismuth is to be separated from small or moderate quantities of lead, and the hydrogen ion concentration of the solution should not be lower than that corresponding to a pH of 1.7.

Basic bismuth formate is slightly soluble in sodium salts in general, and in sodium formate in particular. For this reason ammonium salts have replaced sodium salts used in earlier procedures. An additional advantage in the use of ammonium salts is to prevent contamination of the bismuth formate precipitate by sodium salts.

The results obtained in the analysis of bismuth-lead mixtures of different composition is shown in table 5.

Determination of mercury, arsenic and lead. Mercury may be determined as the metal after reduction of its salts with formic acid. Certain other metals such as copper, which usually interfere, form soluble salts which can be removed by washing.[5]

Formic acid prevents precipitation of small quantities of mercury by hydrogen sulfide, but makes possible instead the formation of a colored colloidal suspension which is suitable for the colorimetric determination of small quantities of mercury.[6]

Procedure. To the solution to be analyzed add 1 per cent of formic acid and saturate with hydrogen sulfide. Compare in a colorimeter with a standard solution containing 1 part of mercuric chloride in 10,000 parts by weight of water. The standard solution is treated with formic acid and hydrogen sulfide in the same way as the unknown. This procedure is sensitive to about 75 parts of mercury in 100,000 parts of water. Differences of 1 part in 100,000 can be detected.

Arsenic and lead may be determined in a similar manner.

Determination of zinc. Zinc is precipitated from a solution containing zinc, iron, cobalt and nickel by converting the metals to the formates and treating with hydrogen sulfide. A large quantity of free formic acid is necessary to prevent simultaneous precipitation of other metals.[7] The following procedure is described by Berg[8,9]

Procedure. Treat the solution containing about 0.1 per cent ZnO and 1 per cent formic acid with hydrogen sulfide. A single precipitation is sufficient to separate zinc from nickel and iron, but in the presence of cobalt a second precipitation is necessary. Filter immediately after adding hydrogen sulfide in excess, and do not allow the residue to dry on the sides of the beaker. Wash with water containing hydrogen sulfide and formic acid.

TABLE 5.—SEPARATION OF LEAD AND BISMUTH WITH AMMONIUM FORMATE

Bismuth Used mg.	Bismuth Found		Lead Used	Lead Found	
	Original mg.	Duplicate mg.		Original mg.	Duplicate mg.
0.5	0.48	0.50	20 g.	Not Determined	Not Determined
1.0	0.99	0.96	20 g.	Not Determined	Not Determined
10.0	9.9	9.8	100 mg.	99.7	99.7
20.0	19.6	20.0	100 mg.	99.8	99.6
50.0	49.7	49.7	100 mg.	99.6	99.9
50.0	49.9	49.8	20 g.	Not Determined	Not Determined
100.0	99.8	99.6	300 mg.	299.3	299.5
100.0	100.0	99.7	20 g.	Not Determined	Not Determined
200.0	199.5	199.9	500 mg.	499.2	500.1
300.0	299.9	300.2	1000 mg.	1000.3	1000.2
300.0	300.3	299.6	20 g.	Not Determined	Not Determined

Detection of tungsten. Tungsten may be detected by fusing the sample with sodium formate and lithium carbonate. Tungsten is detected by the formation of a lithium-tungsten bronze.[10]

Separation of tungsten and molybdenum. Molybdenum may be separated from tungsten by precipitating with hydrogen sulfide in the presence of a buffer consisting of ammonium formate, tartaric acid and formic acid and having a pH of 2.9.

Procedure. Dissolve a mixture of sodium tungstate and sodium molybdate in 10-15 ml. of water and mix with 10 ml. of 50 per cent ammonium formate solution, 10 ml. of 30 per cent tartaric acid solution, 100 ml. of water saturated with hydrogen sulfide at 0° C. and 10 ml. of 2 N formic acid. Digest at 60° C. for one hour, add a little ashless filter paper pulp and 10 ml. of 24 N formic acid. A pure precipitate of MoS_3 is obtained, and upon ignition at 550° C. a residue of pure MoO_3 is formed.

Recover tungsten from the filtrate by evaporating to a small volume and heating with 25 ml. of concentrated nitric acid to oxidize the tartaric acid and ammonium salt. Then dilute the mixture with 100 ml. of water, treat with 5 ml. of a solution containing 12.5 g. of cinchonine in 100 ml. of 6 N hydrochloric acid, and digest on a hot plate for 2 hours.[11] For complete details of the determination, see section on cinchonine.

Determination of platinum. Platinum is often precipitated as the sulfide with hydrogen sulfide and ignited and weighed as metallic platinum. This method is made more accurate by dissolving the residue obtained by ignition of the sulfide in aqua regia and precipitating platinum with sodium formate in a solution buffered with sodium acetate. This precipitate is then ignited and weighed as platinum.[17]

Procedure. Dissolve the residue obtained by the ignition of platinum sulfide in aqua regia, and decompose the nitrogen compounds by adding hydrochloric acid and evaporating to a small volume. Filter the solution into a clean unetched beaker and wash the filter with 1:99 hydrochloric acid. Dilute to 100 ml., heat to boiling, and add a solution containing 3 g. of sodium acetate and 1 ml. of formic acid for each 0.25 g. of platinum. Boil gently until the supernatant liquid is colorless and the precipitate is well coagulated, and then filter. Wash the mixture with hot 1 per cent ammonium chloride solution and ignite strongly in air. Leach, wash, and again ignite and finally weigh as metallic platinum.

Determination of palladium. From a slightly acid solution of palladous choride, metallic palladium is quantitatively precipitated by the reducing action of sodium formate:[18]

Procedure. To a fairly dilute solution of palladous chloride add a solution of sodium formate. Cover with a watch glass and heat the mixture carefully over a free flame. Carbon dioxide is evolved during the reaction and palladium is precipitated as a fine black powder. Since the finely divided metal is appreciably soluble in hydrochloric acid, the excess acid is neutralized with sodium carbonate after the evolution of gas has ceased. Sufficient sodium carbonate is added to make the solution neutral or only faintly alkaline. Filter, wash with hot water, and ignite the moist precipitate in a porcelain crucible. Cool and weigh as metallic palladium.

Determination of copper. Copper salts are quantitatively reduced to metallic copper with potassium formate while cadmium salts are not similarly affected. This makes possible the quantitative separation of copper and cadmium.[14]

Procedure. To each 1 g. of sample add 7.5 g. of potassium formate and evaporate the solution on a hot plate until metallic copper begins to separate. Then heat for 90 minutes in an oven at 150-160° C. At the end of this time all the copper salt is reduced to the metal while the cadmium remains unchanged. Extract with water, and filter through a weighed Gooch crucible. Wash the copper precipitate with water, alcohol, and then ether, dry at 75° C., and weigh as copper.

Results obtained in determining copper with potassium formate are given in table 6.

TABLE 6.—REDUCTION OF COPPER WITH POTASSIUM FORMATE

$CuSO_4 \cdot 5H_2O$ g.	Copper by Reduction		Copper by Electrolysis Per Cent
	g.	Per Cent	
1.0658	0.2654	24.90	24.93
0.8750	0.2180	24.92	24.93
1.1147	0.2778	24.92	24.93
0.8474	0.2112	24.92	24.93

Determination of gold. Formic acid is used as a source of carbon monoxide, which reacts with chloroauric acid to give a color which may be used for the determination of small quantities of gold. The determination is carried out by moistening strips of paper with standard gold solutions and the unknown and exposing to the action of carbon monoxide.[15]

Detection and determination of silver. Metallic silver is formed by the reduction of silver salts with formic acid.[16] This reaction takes place according to the following equation:

$$2AgNO_3 + 5HCO_2H \rightarrow N_2O + 5H_2O + 2Ag + 5CO_2$$

Determination of manganese. Formic acid is used as the electrolyte in the electrolytic determination of manganese, and its separation from iron and zinc. Formic acid and sodium formate are added to the manganese solution, and the manganese is deposited quantitatively as the peroxide.[17]

Manganese can be separated from nickel and cobalt by a procedure which depends upon the fact that manganese sulfide is soluble in acetic and formic acid.[18]

Procedure. Dilute the solution containing about 0.1 g. of cobalt or nickel to 200 ml. and add 4 g. of ammonium chloride. Heat and precipitate with ammonium sulfide, avoiding an excess of this reagent. Allow the mixture to cool, add 1 N formic acid until the solution contains about 1 per cent free acid, and then treat with hydrogen sulfide. Manganese and iron, if present, dissolve as the formates while cobalt and nickel sulfides remain undissolved. The separation of cobalt and nickel from manganese is fairly accurate, but the method is not satisfactory for separating cobalt and nickel from iron.

Determination of iron. Iron may be separated from manganese nickel, cobalt and zinc by precipitating as basic ferric formate: [19]

Procedure. To the acid solution containing ferric iron add 2 moles of ammonium chloride for each atom of iron present and evaporate almost to dryness on a water-bath. Break up the mass with a stirring rod and dry for a short time. Dissolve in water and add a quantity of ammonium formate equal to about twice that required by theory. The ammonium formate is added in the form of an aqueous solution. Dilute the mixture with water, but keep the volume such that the amount of ammonium formate does not fall below 1:800. Heat until the iron begins to precipitate, and then nearly neutralize with dilute ammonium hydroxide. Heat for 1 minute and filter off the basic ferric formate. Wash with dilute ammonium formate, dry, ignite to the oxide and weigh.

Determination of indium. Indium may be deposited electrolytically on platinum by the electrolysis of an indium salt solution in the presence of formic acid. This method is sufficiently accurate to be used for the atomic weight determination of indium.[20]

Detection of rhenium. Noddack [21] has used formic acid to precipitate rhenium from solutions of its salts. By the evaporation of the rhenium salt with formic acid, the black finely divided metal is not formed but the original white compounds is colored blue.[22]

Detection of cerium. Behrens and Kley [23] have used formic acid for the detection of cerium, but Wenger and co-workers [24] do not recommend its use.

Determination of nitric acid. Nitric acid may be determined by a method based on the reaction between a nitrate and formic acid:

$$2KNO_3 + 6HCO_2H \rightarrow N_2O + 4CO_2 + 5H_2O + 2HCO_2K$$

By measuring the volumes of gases evolved in this reaction, the quantity of nitrate may be determined: [25,26]

Procedure. Heat 0.1-0.3 g. of nitrate with 5 ml. of formic acid, and collect the gases evolved over mercury in an eudiometer tube of 200-250 ml. capacity. Read the total volume of gas, then add 2 ml. of concentrated potassium hydroxide and shake, and again read the gas volume. The first volume corresponds to the total volume of carbon dioxide and nitrous oxide, while the second volume corresponds to nitrous oxide only. Calculate the gas volumes to 0° C., and read from a prepared table the corresponding weight of nitrate.

Molinari[27] has not regarded the above method as satisfactory, but Quartaroli,[28] who originally proposed the method, states that with proper precautions results accurate to 0.5 per cent may be obtained.

Vernazza[29] has worked out a titrimetric method for the determination of nitric acid which is based on the reduction of the latter by formic acid in the presence of sulfuric acid to nitrosyl sulfuric acid, and titrating this compound with iodine or potassium permanganate according to the method of Lunge:

Procedure. Dissolve about 0.05 g. of the nitrate in 5-6 ml. of concentrated sulfuric acid, and add 1 drop of a 1 per cent solution of iodine in concentrated sulfuric acid. Then add 0.1 ml. of formic acid and shake well. When the reaction has slowed down, heat the mixture on a water bath to remove the excess formic acid, and titrate the nitrosyl sulfuric acid formed with 0.1 N potassium permanganate.

The relationship between nitric acid and nitrosyl sulfuric acid is shown by the following equation:

$$HNO_3 + HCO_2H + mH_2SO_4 \rightarrow CO_2 + H_2O + SO_2(OH)ONO + (m-1)H_2SO_4$$

Nitrosyl sulfuric acid reacts with water according to the following equation:

$$SO_2(OH)ONO + H_2O \rightarrow H_2SO_4 + HNO_2$$

and nitrous acid reacts with potassium permanganate as follows:

$$5HNO_2 + 2KMnO_4 + 3H_2SO_4 \rightarrow 5HNO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O$$

The permanganate titration is carried out as follows:

Place 150 ml. of water and 10 ml. or more of 0.1 N potassium permanganate solution in a 250-ml. flask, and add dropwise and with constant stirring the nitrosyl sulfuric acid solution prepared as directed above. Wash out the flask in which it was contained with acidified 0.1 N potassium permanganate and finally with water. The mixture must be purple in color, thereby indicating an excess of permanganate. Decolorize with a measured quantity of 0.1 N ferrous sulfate, and finally titrate to the appearance of a pink color with 0.1 N potassium permanganate. One ml. of 0.1 N $KMnO_4$ is equivalent to 0.0019 g. of N_2O_5.

Ammonium salts do not interfere in this determination unless present in quantities greater than 5-6 times that of the nitric acid.

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FUMARIC ACID

Synonym: *trans*-Butendioic acid

$C_4H_4O_4$ Mol. Wt. 116.07 Beil. Ref. II, 737.

$$HO_2C{-}CH{=}CH{-}CO_2H$$

Use: Separation of thorium from cerium, lanthanum, neodymium, praseodymium. Standardization of sodium hydroxide solutions.

Fumaric acid is a white crystalline compound. It melts at 282° C. in a sealed tube, although it sublimes above 200° C. in an open vessel. It is soluble in 150 parts of cold water, but is more soluble in hot water. It is slightly soluble in alcohol and most organic solvents.

Preparation: Place 45 g. of sodium chlorate, 0.2 g. vanadium pentoxide, and 100 ml. of water in a 500-ml. flask and equip with a condenser and a separatory funnel. Heat the contents of the flask to 70-75° C. and slowly add with agitation 20 g. of furfural. Heat with occasional shaking for 10 hours, and then allow the mixture to stand at room temperature for 24 hours. Filter with suction, and dry in air. Purify by recrystallization from 1 N hydrochloric acid. The melting point is 282-4° C. in a sealed tube.[1]

Separation of thorium. Thorium is precipitated quantitatively from a 40 per cent alcoholic solution by the addition of fumaric acid. Since no precipitation occurs when fumaric acid is added to cold solutions containing cerium, lanthanum, praseodymium and neodymium, fumaric acid serves as a suitable reagent for the separation of thorium from these metals. Traces of these metals may, however, be carried down with the thorium precipitate, but this may be removed by a single precipitation.[2,4]

Standardization of sodium hydroxide solutions. A solution of sodium hydroxide may be standardized by titrating against fumaric acid with about the same accuracy as that obtained by standardizing hydrochloric acid by precipitating as silver chloride. Fumaric acid has also been used to standardize solutions of potassium permanganate, but its use offers no advantages over sodium oxalate. The acid cannot be used with ammonium hydroxide, and it is not satisfactory for iodometric work.[3]

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FUROIC ACID

Synonym: Pyromucic acid, furan-2-carboxylic acid

$C_5H_4O_3$ Mol. Wt. 112.08 Beil. Ref. XVIII, 272.

$C_4H_3O—CO_2H$

Use: Alkalimetric standard and a preservative for analytical solutions.

Furoic acid is a white, crystalline solid. It melts at 131° C., boils at 230-232° C., and decomposes at about 250° C. It begins to sublime at 100° C. It is soluble in 28 parts of cold water, and 4 parts of boiling water. It dissolves readily in alcohol and ether.

Preparation: Dissolve 50 g. of sodium hydroxide in 500 ml. of water and cool. Transfer this solution to a 2-liter beaker, which is supported on a wire gauze to permit subsequent heating. Support above the beaker a dropping funnel, thermometer, and efficient stirrer. Add to the solution in the beaker a quantity of chipped ice and 25 g. of freshly distilled furfural. While stirring rapidly, add dropwise, though rapidly, a solution prepared by dissolving 34 g. of potassium permanganate in 600 ml. of water. Add chipped ice from time to time to keep the temperature between 10 and 15° C. While still stirring, heat the mixture nearly to boiling, and after 30 minutes filter through a Buchner funnel. Boil the residue of the oxide of manganese with 200 ml. of water and filter, and combine the two filtrates.

To the combined filtrates, add 90 ml. of concentrated hydrochloric acid, and carefully add acid or base as necessary to make the reaction slightly acid. Evaporate the mixture rapidly to a volume of 500 ml. over a free flame, and then on a water bath to a volume of 250 ml. Add a little water to dissolve any crystals which form, and purify by digesting for a time with charcoal. Filter hot, and to the filtrate add a slight excess of hydrochloric acid, but do not add enough to precipitate sodium or potassium chloride. The liquid sets to a mass of nearly white crystals. Cool the mixture, filter with suction, and wash the precipitate with 50 ml. of ice water. Extract the mother-liquor with three 50-ml. portions of ether, and recover the extracted acid by evaporation of the solvent. Recrystallize from hot water, using 5 ml. for each gram of acid.[1,4]

Use as a primary standard. Furoic acid may be used as a primary standard with about the same accuracy as obtained with benzoic acid. Among the advantages claimed for this reagent are: (1) the ease with which it may be purified; (2) its solubility in water; (3) its stability; (4) its lack of hygroscopicity, and (5) its moderately high equivalent weight, which is 112.08.[2]

Use as a preservative for analytical solutions. A 0.1 per cent solution of sodium furoate is used as a preservative for sodium thiosulfate, starch, or tannic acid solutions. Reagents so treated remain unchanged over long periods of time.[3]

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MALEIC ACID

Synonym: Toxilic acid, *cis*-butendioic acid

$C_4H_4O_4$ Mol. Wt. 116.07 Beil. Ref. II, 748.

$$HO_2C—CH=CH—CO_2H$$

Use: Alkalimetric standard.

Maleic acid is a white crystalline solid which possesses a characteristic astringent taste. It melts at 138-139° C., and boils at about 135° C. with decomposition. It dissolves readily in water or alcohol, but only slightly in benzene.

Preparation: Mix malic acid at room temperature with an excess of acetyl chloride, and heat the mixture under reflux on a water bath. Distill at ordinary pressure to expell acetyl chloride, acetic acid and hydrogen chloride. Crude maleic anhydride remains behind. Mix with phosphorus pentoxide and sublime *in vacuo* at 10-15 mm. The anhydride comes over at 120-130° C. Dissolve in water and carefully evaporate to obtain pure crystals of maleic acid.[1]

Acidimetric standard. Maleic acid may be used for the standardization of sodium hydroxide solutions. The reagent may be purified by recrystallizing once from water and drying to constant weight over sulfuric acid, or in an oven at 90° C. for two hours. Lange and Kline [2] report that results using this reagent are as accurate as those obtained in standardizing hydrochloric acid solutions by precipitating as silver chloride. Maleic acid may also be used for the standardization of potassium permanganate solutions, but offers no advantage over the more readily available sodium oxalate.

1. Anschütz, *Ber.* **14**, 2791 (1881).
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MALONIC ACID

$C_3H_4O_4$ Mol. Wt. 104.06 Beil. Ref. II, 566.

$$HO_2C—CH_2—CO_2H$$

Uses: Detection of beryllium.

Determination of copper. Alkalimetric standard.

Malonic acid is a white crystalline solid. It melts at about 135° C. with decomposition. One gram of the solid dissolves in 0.65 ml. of water, 2 ml. of alcohol, 1.1 ml. of methyl alcohol and 13 ml. of ether.

Preparation: In a 5-liter flask, dissolve 500 g. of chloroacetic acid in 700 ml. of water. Warm to 50° C. and neutralize with 290 g. of anhydrous sodium carbonate. Allow the mixture to cool to room temperature. Meanwhile, dissolve 294 g. of sodium cyanide in 750 ml. of water and warm to 55° C. Cool to room temperature and add the sodium chloroacetate solution with rapid mixing and cooling under the tap. When the solutions are completely mixed, discontinue the cooling and allow the temperature to rise. When it reaches 95° C., cool by adding 200 ml. of ice water, and repeat, if necessary, until the temperature no longer rises. Then heat the mixture 1 hour on a steam bath.

Cool to room temperature and slowly dissolve in the mixture 240 g. of U.S.P. sodium hydroxide. When the reaction is complete, heat on a steam bath under a hood. Heat for 3 hours and remove the last traces of ammonia by bubbling steam through the mixture for an additional hour.

Dissolve 600 g. of anhydrous calcium chloride in 1.8 liters of water and heat to 40° C. Add this solution slowly and with rapid mixing to the sodium malonate solution. Allow to stand 24 hours. Decant the supernatant liquid, and wash the calcium malonate 4-5 times by decantation with 500-ml. portions of cold water. Filter with suction, and suck as dry as possible. Dry in air, or at 40-45° C. to constant weight.

Place the dry calcium malonate in a 3-liter round bottom flask and add from 750-1000 ml. of alcohol-free ether, or a sufficient quantity to form a paste that can be stirred. Surround the flask with an ice bath, and treat the well-stirred salt with 1 ml. of 12 N hydrochloric acid for each gram of salt. Add the acid slowly through a dropping funnel. Transfer the solution to a continuous extractor, and extract with ether until no more pure malonic acid is obtained. The product obtained from the undried ether solution by concentration, filtration and drying in air, melts at 130° C.[1,6]

Detection of beryllium. Beryllium may be detected by adding a tiny crystal of potassium malonate to a drop of the solution to be tested and concentrating by evaporation. A characteristic crystalline solid forms with beryllium. This method does not appear to be as satisfactory as that with potassium oxalate, which is carried out similarly.[2]

Determination of copper. Malonic acid can be used to eliminate interference by iron in the electrolytic determination of copper.[3]

Alkalimetric standard. Malonic acid may be used satisfactorily for the standardization of solutions of bases.[4,5] The acid is recrystallized from boiling water and dried to constant weight over sulfuric acid in a desiccator.

1. M. Conrad, *Ann.* **204**, 126 (1880).
2. H. S. Booth and S. G. Frary, *J. Phys. Chem.* **36**, 2641-50 (1932); *C.A.* **26**, 5870 (1932).
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4. I. K. Phelps and L. H. Weed, *Am. J. Sci.* **26**, 138-42 (1908).
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MYRISTIC ACID

$C_{14}H_{28}O_2$ Mol. Wt. 228.36 Beil. Ref. II, 365.

$$CH_3(CH_2)_{12}CO_2H$$

Use: Determination of calcium and magnesium (hardness of water).

Myristic acid is obtained from nutmeg butter or ucuhuba fat. It consists of white, odorless crystals which melt at 52-53° C. and boil at 250.5° C. at 100 mm. It is insoluble in water, sparingly soluble in cold alcohol, but is soluble in methyl alcohol, benzene, chloroform and ether.

Determination of calcium and magnesium. Masters and Smith [1,2] claim that soaps prepared from saturated fatty acids are more satisfactory than those from unsaturated acids for the determination of calcium and magnesium. They report that potassium myristate solutions are stable and give accurate results with calcium and magnesium salts, either alone or together. The end-point in the titration, however, is unsatisfactory at elevated temperatures. Zink and Hollandt [3] have studied the use of myristate solutions, but do not find them more satisfactory than solutions of palmitate.

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2. H. Masters and H. L. Smith, *Proc. Chem. Soc.* **29**, 76 (1913).
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NAPHTHENIC ACID

Synonym: Hexahydrobenzoic acid, cyclohexanecarboxylic acid

Use: Detection of cobalt, copper, hydrogen peroxide and iron.

Determination of copper.

The term "Naphthenic acid" is frequently applied to hexahydrobenzoic acid, $C_6H_{11}—CO_2H$, which consists of transparent crystals. These melt at 30-31° C. and boil at 233° C. The compound is slightly soluble in water, but is freely soluble in alcohol, chloroform, ether and petroleum ether. Kharichkov,[1] who is responsible for most of the applications of naphthenic acid in analytical chemistry, reports that naphthenic acid is an isomer of pentamethylenecarboxylic acid.

The material actually used in these reactions probably consisted of a mixture of the mono-, di-, and tricarboxylic acids of cyclopentane.

Detection of iron. According to Kharichkov[2] a solution of naphthenic acid in benzene or petroleum ether extracts ferrous iron quantitatively from neutral or faintly acid solutions of ferrous salts. The upper layer is chocolate-brown in color if iron is present, while the lower layer gives no test when treated with potassium ferricyanide. Many impurities such as unsaturated acids prevent this reaction. Lutshinnskii[3] has studied this reaction and has found that ferrous naphthenate (free from the ferric salt) is insoluble in benzene or ligroin, while a solution of the ferric salt of this reagent is yellow in color. After the ferrous compound is oxidized a brown color develops.

Pyhälä[4] has concluded that the naphthenic acids which show the Kharichkov reaction are not pure, but contain sodium salts of the acids. Pure naphthenic acids, regardless of their molecular weight, do not give this reaction. According to these studies the chocolate-brown color produced with ferrous sulfate is caused by the ferric salts of the naphthenic acid.

Kharichkov[1] recommends preparing the pure reagent by adding a mineral acid to a solution of a naphthenic acid soap, but Pyhälä reports that naphthenic acid prepared in this manner contains sodium naphthenates in colloidal form.

Detection of copper and cobalt. Naphthenic acids, which are obtained in the refining of kerosene, react with salts of the heavy metals to give highly colored salts which are soluble in ether and benzene.[5,6]

When an aqueous solution of copper sulfate is shaken with an 8 per cent solution of naphthenic acid in benzine, an intensely green colored precipitate is formed. Cobalt nitrate and cobalt chloride yield raspberry-red colors even in the presence of nickel. With nickel a light green compound is formed. By shaking the benzine layer obtained in the reaction with cobalt or nickel salts with hydrogen peroxide, a greenish-brown color appears if cobalt is present, while with nickel the color remains unchanged.

Determination of copper. Muller and Burtsell[8] have studied the possibility of using the reaction between naphthenic acid and copper for the colorimetric determination of the latter. They claim that this method is less satisfactory than others which have been reported.

Detection of hydrogen peroxide. A benzine solution of naphthenic acid is colored rose when shaken with a neutral or weakly acid solution of a cobalt salt. This color is changed by oxidation to a dark brown or olive green.[7] To detect hydrogen peroxide by this reaction proceed as follows:

Procedure. Immerse a strip of filter paper into a benzine solution of the cobalt salt of naphthenic acid and allow to dry. The resulting rose color changes to a characteristic olive-green when the paper is moistened with a dilute solution containing as little as 0.03 per cent hydrogen peroxide.

Ozone does not affect this reagent.

1. K. V. Kharichkov, *Chem.-Ztg.* 35, 671 (1911); *C.A.* 5, 2788 (1911).
2. K. V. Kharichkov, *Chem.-Ztg.* 35, 463 (1911); *C.A.* 5, 2476 (1911).
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4. E. Pyhälä, *Chem.-Ztg.* 36, 869-70 (1912); *C.A.* 6, 3381 (1912).
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6. K. V. Kharichkov, *Petroleum.* 5, 517; *C.A.* 4, 1279 (1910).
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8. R. H. Muller and A. T. Burtsell. *Mikrochem. ver. Mikrochim. Acta.* 28, 209-28 (1940); *C.A.* 34, 7776 (1940).

β-NAPHTHOIC ACID

Synonym: Naphthalene-2-carboxylic acid

$C_{11}H_8O_2$ Mol. Wt. 172.17 Beil. Ref. IX, 656.

$C_{10}H_7—CO_2H$

Use: Detection of boron and cerium.

β-Naphthoic acid consists of white plates or needles. It melts at 184-185° C., and boils above 300° C. It is only slightly soluble in hot water but is soluble in alcohol and ether.

Preparation: Dissolve 184 g. of sodium hydroxide in 300-400 ml. of water contained in a 3-liter flask, and add sufficient ice to make the total volume about 1.5 liters. Cool the mixture to below 0° C. by means of a salt-ice bath and pass chlorine into the solution until it is neutral to litmus. The mixture is kept cold during the addition of chlorine. Add 34 g. of sodium hydroxide dissolved in 50 ml. of water. Warm the solution to 55° C., and add 85 g. of methyl-β-naphthylketone. Stir vigorously until the exothermic action begins, and keep the temperature at 60-70° C. by frequent cooling in an ice-bath until the temperature no longer tends to rise. This usually requires about 30-40 minutes. Stir the solution for an additional 30 minutes and add a solution of 50 g. of sodium bisulfite in 200 ml. of water to destroy the excess hypochlorite. Allow to cool to room temperature, transfer the mixture to a 4-liter beaker, and carefully acidify with 200 ml. of concentrated hydrochloric acid. Filter through a Buchner funnel, wash with water, and remove as much of the water as possible by suction. Dry the crude product, and recrystallize from 600 ml. of 95 per cent alcohol.[1]

Detection of cerium. Ammonium naphthoate reacts with solutions of tetravalent cerium to form a dark lilac-black, voluminous precipitate. This precipitate is insoluble in strong acids, but becomes flaky and reddish-brown in color when treated with ammonium hydroxide. Shemyakin and Belokon[2] have used this reaction for the detection of cerium. It is not, however, sufficiently sensitive to use as a spot test, and Wenger and Duckert[3] report unfavorably on this test because of its lack of sensitivity. Trivalent cerium, thorium, titanium, zirconium, praseodymium and columbium do not give this reaction.

Detection of boron. Salicylic acid has been used to improve the turmeric test for boric acid (page 128). Michel[4] reports that β-naphthoic acid may be used in place of salicylic acid, but that only these two acids are satisfactory.

1. *Organic Synthesis,* Collective Vol. II, p. 428, John Wiley New York (1943).
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3. P. Wenger, R. Duckert and Y. Rusconi, *Helv. Chim. Acta.* **25**, 1547-52 (1942).
4. F. Michel, *Mikrochem. ver Mikrochim. Acta.* **29**, 63-72 (1941) ; *C.A.* **35**, 5412 (1941).

OLEIC ACID

$C_{18}H_{34}O_2$ Mol. Wt. 282.45 Beil. Ref. II, 463.

$$CH_3(CH_2)_7—CH=CH—(CH_2)_7—CO_2H$$

Use: Detection of ammonia, calcium and copper.

Determination of calcium, magnesium and sulfur.

Pure oleic acid is a colorless, or nearly colorless liquid above 5-7° C. Its sp. gr. is approximately 0.895. It boils at 286° C. (100 mm.) and solidifies at 4° C. to a crystalline mass. On exposure to air, especially when not pure, oleic acid is oxidized, and acquires a yellowish color. The acid is insoluble in water, but dissolves in alcohol, benzene, chloroform, and ether. The acid of commerce usually contains 7-12 per cent of saturated acids and some unsaturated acids.

Determination of calcium. In extremely dilute solutions, containing 0.005-0.01 mg. of calcium in 50 ml., calcium can be determined by the pale yellow color of the colloidal solution of calcium oleate, which is formed upon the addition of potassium oleate.[1]

Reagents. *Reagent A:* Dissolve 20 g. of Rochelle salt and 7.5 g. potassium hydroxide in 100 ml. of water.

Reagent B: Dissolve 2 g. of oleic acid and 0.5 g. of potassium hydroxide in 600 ml. of alcohol and dilute to 1 liter.

Procedure. Place the sample in a 50-ml. volumetric flask and dilute to about 45 ml. In a second 50-ml. volumetric flask, place 5 ml. of a standard calcium solution containing 0.02 mg. of calcium in 1 ml. of 0.05 N nitric acid. This is prepared as described in the determination of calcium with stearic acid (page 83). Dilute the standard to almost 45 ml. To each flask add 1 ml. of reagent A and mix well. Then add to each 1 ml. of the oleic acid solution (reagent B) and again mix. Dilute to 50 ml., again mix, allow to stand for 1 hour and compare nephelometrically.

Since magnesium gives a similar color it must be removed. This is done as follows: evaporate the solution to dryness with nitric acid in a platinum dish; heat to redness to convert the calcium and magnesium compounds to the oxides; and then dissolve calcium oxide in water free of carbon dioxide.

In the nephelometric determination of calcium by the stearate method, greater uniformity of dispersion and stability of the colloid are obtained by the use of a modified Leiman reagent containing oleic acid.[2] This reagent is prepared as follows:

Reagent. Dissolve 4 g. of stearic acid and 0.5 g. of oleic acid in 425 ml. of 95 per cent alcohol on a water bath at moderate temperature. To this solution add a second solution prepared by dissolving 20 g. of ammonium carbonate in 100 ml. of water. Cool the mixture, add 425 ml. of alcohol, 50 ml. of water, and 20 ml. ammonium hydroxide (d. 0.9) and filter.

This reagent may be used for the determination of calcium in slags.

Procedure. Dissolve the material in the usual manner, and precipitate the trivalent metals as the hydroxides. Filter, precipitate calcium from the filtrate as the oxalate, again filter, wash, and ignite gently in a platinum crucible. Dissolve the calcium oxide in a few drops of nitric acid and water, and evaporate the solution to dryness. Dissolve the residue in 50 ml. of water, and to a small aliquot add 10 ml. of water and sufficient reagent to make the volume 50 ml. Digest the mixture for 15 minutes at 30-40° C. and cool. Proceed with the determination using a photonephelometer. Best results are obtained at concentrations of 0.02-0.6 mg. of calcium in 50 ml.

Calcium may be determined in milk by a similar method proposed by Kober.[3]

Detection of calcium. Sodium oleate in gelatin, at a pH of 7.2-7.8, may be used to detect as little as 0.0005 mg. of calcium in 1 ml. of solution.[4] The reaction which occurs may be characterized as a stabilized ring reaction. This test is not specific for calcium.

Reagent. The solution is prepared so that the final concentration of gelatin is 5 per cent. Dissolve the gelatin in water with sufficient space left in the tube for the addition of the other ingredients. Add 20 ml. of 0.01 N. sodium oleate. Then add immediately 12.5 ml. of 0.1 N sodium hydroxide or potassium hydroxide solution. Finally, add sufficient sodium hydroxide to bring the pH to 7.4, using phenol red as the indicator.

Procedure. Add 1 ml. of the solution to be tested to 3 ml. of the reagent. A reaction which can be distinguished from that of a control is regarded as a positive test.

Potassium oleate may be used in preparing the reagent, and possesses the advantage of greater clearness.

Determination of magnesium. Like calcium, magnesium may be determined colorimetrically with potassium oleate.[5,6]

Reagent. *Reagent A:* Dissolve 100 g. of ammonium chloride and 9 g. of ammonia in sufficient water to make one liter of solution.

Reagent B: Dissolve 2 g. of oleic acid and 0.5 g. of potassium hydroxide in 600 ml. of alcohol and 400 ml. of water.

Procedure. Treat the solution containing 0.008-0.1 mg. of MgO with 2 ml of the ammonium chloride solution and 1 ml. of the potassium oleate reagent. Dilute the mixture to 50 ml. and allow to stand 2 hours before comparing the resulting color with that produced with known quantities of magnesium. Calcium must be absent, and can be removed as described in the preceding section.[1]

Determination of the hardness of water. Sodium oleate has been used in place of the salts of the fatty acids (stearic acid) for determining the hardness of water, but according to Masters and Smith [7] poor results are obtained due to the precipitation of magnesium oleate. Salts of the saturated fatty acids are more satisfactory.

Detection of ammonia. Herzog [8] has described an interesting method for the microchemical detection of ammonia in flame-proofed paper and fabrics used for stage settings and other decorations.

Procedure. A few fibers of the material to be tested are placed on a microscope slide, and a glass ring 1-3 mm. in height is placed around them. A drop of concentrated sodium hydroxide solution is then placed on the material, and the ring is covered with a glass cover slide on the under side of which a drop of oleic acid has been placed. After a time the oleic acid is observed with a microscope. If ammonia is present, the surface of the drop of acid presents curious wrinkles and furrows, the so-called myelin forms described by Senft.[11] Eventually the drop spreads over the glass and becomes opaque due to the formation of ammonium oleate. As little as 1γ of NH_3 can be detected in this manner.

Detection of copper. The blue color which forms with oleic acid may be used as a sensitive test for copper.[9] This reaction, however, does not seem to be very satisfactory. When a drop of oleic acid is added to a solution containing copper, a day or two may elapse before the color develops. Color formation can be hastened by stirring or boiling, but the formation of an emulsion must be avoided. The pH should be between 5.0-8.0.

Sulfur analysis. Filippova and Markova [10] have made a study of Hengel's and Robinson's methods for the dispersion methods of sulfur analysis, and claim that Robinson's method gives better reproductibility of results. They have found also that sodium oleate is the best stabilizer for sulfur suspensions when used in quantities of 0.2 g. per 100 ml.

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4. S. Amberg, J. Landsbury, and F. Sawyer, *J. Am. Chem. Soc.* **50**, 2630-33 (1928); *C.A.* **22**, 4404 (1928).
5. A. Gregoire and T. Sola, *Bull. soc. Chim. Belg.* **32**, 131-6 (1923): *C.A.* **17**, 1931 (1923).
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7. H. Masters and H. L. Smith, *J. Chem. Soc.* **103**, 992-8 (1913); *C.A.* **7**, 3377 (1913).
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10. A. G. Filippova and G. A. Markova, *Zavodskaya Lab.* 10, 31-4 (1941); *C.A.* **35**, 5060 (1941).
11. M. E. Senft, *Pharm. Post.* **40**, 265-71, 287-89, 304, 319-21; *C.A.* 1, 2159 (1907).

OXALIC ACID

$C_2H_2O_4 \cdot 2H_2O$ Mol. Wt. 126.07 Beil. Ref. II, 502

$$HO_2C—CO_2H$$

Use: Detection of beryllium, bromate, calcium, cerium, chromium, gold, iridium, lanthanum, magnesium, manganese, nitrite, osmium, palladium, platinum, sodium, strontium, thorium and yttrium.

Determination of aluminum, antimony, beryllium, calcium, cadmium, cerium, chromium, cobalt, columbium, copper, gold, iron, lead, manganese, nickel, rare earths, silver, strontium, tantalum, thorium, tin, titanium, uranium and zinc.

Standard in acidimetry, alkalimetry and oxidimetry.

Oxalic acid is a colorless crystalline solid. It occurs as the dihydrate, which melts at 99.5-101.5. It becomes anhydrous at 189° C. and can be dehydrated by careful drying at 100° C. One gram of the solid dissolves in about 7 ml. of cold water or 2 ml. of boiling water. One gram dissolves in 2.5 ml. of cold alcohol and 100 ml. of ether, but it is insoluble in benzene and chloroform.

Precipitation of metallic ions. Oxalic acid is widely used in analytical chemistry as a precipitant for many cations with which it reacts to form insoluble oxalates. When ammonium oxalate is added to a slightly alkaline solution having a pH of approximately 8.0, and which contains all ions, the following are completely precipitated, or nearly so[1]: calcium, strontium, scandium, yttrium, lanthanum, the rare earths, actinium, iron, gold, bismuth, indium, tin, columbium and tantalum. The following are incompletely precipitated: lithium, beryllium, magnesium, barium, radium, titanium, zirconium, hafnium, thorium, manganese, cobalt, nickel, mercury, thallium and lead. The following may be precipitated under certain conditions: vanadium, tungsten, carbon, phosphorus, arsenic and fluorine.

By adding ammonium oxalate to a solution that has been made acid to thymol blue (pH3-4), and which contains all elements, the following are completely precipitated, or nearly so[1]; calcium, strontium, scandium, yttrium, lanthanum, rare earths, actinium, thorium and gold. The following are incompletely precipitated under these conditions: barium, tantalum, manganese, cobalt, nickel, copper, silver, zinc, cadmium, tin, lead and bismuth.

Wagenaar[2] has determined the delicacy of a number of precipitation tests for the metals with ammonium oxalate. These results are given in Table 7.

TABLE 7.—DETECTION OF METALS AS OXALATES

Metal	Quantity of Oxalate That Can Be Detected (mg. of metallic oxalate)	Dilution
Strontium	0.01	1:200
Zinc	0.002	1:500
Manganese	0.002	1:1000
Cadmium	0.005	1:500
Bismuth	0.002	1:500
Antimony	0.005	1:200
Lead	0.002	1:500
Silver	0.002	1:500

In the following sections are given typical examples of the use of oxalic acid in analytical procedures, and many of these are based upon the formation of metal oxalates.

Detection and determination of calcium. Ammonium oxalate reacts with calcium salts in neutral or alkaline solutions to yield a precipitate of calcium oxalate. When formed in cold solutions, the oxalate consists of extremely fine crystals which are difficult to filter, but when formed from hot solutions larger crystals are formed. This reaction has been widely used for the detection of calcium.

One of the best methods for the determination of calcium is based upon the formation of insoluble calcium oxalate. The solution should contain no other cations except magnesium and the alkali metals. If magnesium is present, sufficient ammonium salts should be added to prevent the precipitation of magnesium hydroxide upon making alkaline with ammonium hydroxide. Since a description of this procedure is included in all standard text books of quantitative analysis, no effort has been made to review the voluminous literature describing this method of analysis. The following procedure, however, may be taken as typical of those based upon the precipitation of calcium oxalate.

Procedure. Make the solution to be analyzed slightly acid and heat to boiling. Add a slight excess of hot ammonium oxalate solution, and then add slowly and with stirring sufficient ammonium hydroxide to make the solution neutral. Allow the mixture to stand for about 4 hours and test for completeness of precipitation by adding a little more ammonium oxalate. Decant the clear supernatant liquid through a filter and cover the precipitate with boiling water containing ammonium oxalate. Allow to settle, filter, and repeat the washing by decantation three times. Finally, transfer the precipitate to the filter and wash with a hot, very dilute solution of ammonium oxalate until free from chloride. Ignite the moist filter carefully in a platinum crucible. The precipitate should be heated cautiously at first to prevent a too rapid evolution of carbon dioxide. When the precipitate is perfectly white, cover the crucible and heat strongly over a Meker burner for 20 minutes. Allow to cool to about 100° C. in air and then for an additional 15 minutes in a desiccator. Weigh as CaO. Heat for an additional 10 minutes over the Meeker burner and again weigh.

Calcium may be determined titrimetrically after precipitation as the oxalate.

Procedure. Transfer the moist precipitate of calcium oxalate to a beaker with the aid of a stream of water from a wash bottle, and dissolve the precipitate remaining on the filter by pouring over it hot 2 N sulfuric acid. To the turbid solution in the beaker add 20 ml. of concentrated sulfuric acid, dilute with hot water to a volume of 300-400 ml. and titrate the oxalic acid with 0.1 N potassium permanganate solution. One ml. of N potassium permanganate is equivalent to 20.04 mg. of calcium.

The difference in the solubilities of calcium and magnesium oxalates may be used for the separation of calcium from magnesium.[3] Calcium oxalate is practically insoluble in hot water, while magnesium oxalate is fairly soluble. The solubility of magnesium oxalate is increased by the presence of ammonium chloride and also by a large excess of ammonium oxalate. Twenty grams of ammonium oxalate prevents the precipitation of 2.7 g. of magnesium chloride in 100 ml. of solution.[4] When calcium oxalate is precipitated in the presence of magnesium, some magnesium may be found in the precipitate. Three methods have been proposed for the precipitation of small quantities of calcium in the presence of large quantities of magnesium:

(a) Calcium oxalate is precipitated in the usual way and after filtration is dissolved and reprecipitated two or three times; (b) calcium oxalate is precipitated in the presence of an ammonium salt, using only a slight excess of ammonium oxalate; and (c) calcium oxalate may be precipitated from 100 ml. of solution by the addition of 20 g. of ammonium oxalate.

The following procedure is recommended by Treadwell and Hall:[5]

Procedure. Dilute the slightly acid solution with hot water so that not more than 0.3 g. of either calcium or magnesium is present in 300 ml. of solution. Add 10 g. of ammonium chloride and heat to 80-90° C., and add slowly and with stirring an aqueous solution containing 2 g. of ammonium oxalate. Add ammonium hydroxide until the solution is slightly ammoniacal and allow the mixture to stand for 1 hour. Filter, wash with hot water, and determine calcium as described above.

Ferric hydroxide dissolves readily in a concentrated aqueous solution of oxalic acid. Ferric oxalate does not give a thiocyanate test for iron, but yields an easily filterable precipitate with ammonium hydroxide. It also forms double salts, notably with calcium oxalate, but this compound is easily decomposed by acetic acid, leaving insoluble calcium oxalate. Barlot[6] suggests that this property may be used for the separation of iron from calcium. Instead of precipitating ferric hydroxide first and then calcium oxalate in the usual manner, it is better to add the oxalate to a nearly neutral solution containing ammonium chloride, and then acetic acid to dissolve the aluminum and iron oxalates, leaving insoluble calcium oxalate behind.

Calcium may be determined nephelometrically by precipitating as the oxalate.[7,8] This method is reported to offer some advantages for the determination of small quantities of calcium in biological fluids, since a single determination requires only about 10 minutes. According to Polinkavskii,[9] however, the method does not give satisfactory results due to the large size of the particles. The effect of ammonium salts, the use of an excess of the precipitant, and the order of mixing the reagents also appear to be important. The use of a stabilizer like glycerol or gelatin is necessary.[10] Standards cannot be kept for any length of time. The error reported for this method is approximately 20 per cent. The following procedure may be used for the determination of calcium in blood:

Procedure. Place 2 ml. of blood in a tube and dilute to 8 ml. Mix well, add 1 g. of trichloroacetic acid and shake. Dilute to 10 ml., again mix and filter into a tube which is graduated at 5 ml. Collect exactly 5 ml. of the filtrate, make distinctly alkaline with 1:1 ammonium hydroxide and then make distinctly acid with 30 per cent acetic acid. Add a few crystals of ammonium oxalate and heat to boiling for a few minutes. Cool slightly, add 1 ml. of pure glycerol, and dilute to 15 ml. with water. Mix and compare in a nephelometer with 2 ml. of a standard similarly prepared.

The final determination may be made by duplication as follows: Add 10 ml. of saturated ammonium oxalate solution to each of 2 cylinders, and to each add 1 ml. of concentrated ammonium hydroxide and 1 ml. of 0.1 per cent gelatin. Mix well and add to one cylinder the sample or a suitable aliquot. Dilute to 25 ml. and mix. Adjust the other cylinder by the addition of a standard calcium solution until the volume and reflection are matched.

Calcium may be approximately estimated in water by comparison with standards:[11]

Procedure. Add 1 ml. of 50 per cent acetic acid to 10 ml. of the water to be tested, and then add 1 ml. of a 20 per cent potassium oxalate solution. Mix well and compare after 10 minutes with a series of standards similarly and simultaneously prepared.

Calcium may be determined colorimetrically by a method based on the fact that the red color of a solution of ferric thiocyanate is discharged by oxalates.[12] Calcium is precipitated as the oxalate, which is dissolved in acid and added to a standard solution of ferric thiocyanate. The mixture is diluted to a definite volume and the color of the solution is compared with that of standards containing known quantities of calcium oxalate and ferric thiocyanate. This method is especially suitable for the determination of calcium in blood.[13,14,16-18] Since phosphates also decolorize ferric thiocyanate solution, they must be absent. Magnesium does not interfere in the presence of ammonium salts. Results reported by this method are accurate to about 2 per cent. The following procedure may be used for the determination of calcium in blood.

Reagents. *Ferric thiocyanate reagent:* Mix 5 ml. of 0.3 per cent ammonium thiocyanate solution with 5 ml. of 0.3 per cent ferric chloride solution. Add a few drops of 1:1 hydrochloric acid if necessary to clarify the liquid and dilute to 25 ml. Allow to stand for 30 minutes before using.

Standard calcium solution: Dissolve 0.0630 g. of pure hydrated oxalic acid in water and add 200 ml. of a N hydrochloric acid solution containing 0.0554 g. of anhydrous calcium chloride. Dilute to 1 liter. One ml. of this solution corresponds to 0.02 mg. of calcium.

Procedure. Transfer 2 ml. of clear blood serum to a beaker containing 10 ml. of concentrated nitric acid and heat just below boiling for 2-3 hours. Heat more strongly and evaporate to 0.5 ml. If the mixture is charred, add an additional 10 ml. of concentrated nitric acid and again evaporate. Wash down the sides of the beaker and add 1 drop of 1 per cent phenolphthalein solution. Make slightly alkaline with 1:3 ammonium hydroxide solution and boil 2 or 3 minutes. Add dropwise and with stirring to the hot solution 1 ml. of a 1.25 per cent oxalic acid solution in 0.25 N hydrochloric acid. Allow to cool and add 0.5 ml. of 35 per cent crystallized sodium acetate solution. Allow the mixture to stand overnight and separate the calcium oxalate by centrifuging. Dissolve the precipitate in 0.5 ml. of concentrated nitric acid, add 10 ml. of water and immerse in a boiling water-bath. Stir with a current of air, transfer to a beaker, evaporate to 0.5 ml. and precipitate calcium as described above. If magnesium is not to be determined, the second precipitation is unnecessary.

Filter the calcium oxalate through a Gooch crucible containing alternate layers of filter paper and asbestos. Wash several times with 5 ml. portions of 1 per cent ammonium hydroxide, and then wash once with alcohol made just alkaline with ammonium hydroxide, and finally with ether. Place the Gooch crucible in a beaker and pour into it 10 ml. of 0.2 N hydrochloric acid. Allow to stand for several hours in a covered dish over water to prevent evaporation. Stir the asbestos in the acid and centrifuge.

Transfer a 5-ml. aliquot of the clear supernatant liquid to a small tube and add exactly 2 ml. of the ferric thiocyanate reagent and dilute to 10 ml. with 0.2 N hydrochloric acid. Compare by viewing lengthwise with a series of standard calcium oxalate solutions similarly treated. The color varies inversely with the calcium content.

Detection and determination of strontium. Strontium, like calcium, yields a precipitate with ammonium oxalate, but the strontium salt is somewhat soluble in acetic acid. This reaction has been used for the detection and the determination of strontium.[19,20]

Detection of magnesium. Magnesium yields a precipitate with ammonium oxalate, but the compound is much more soluble in ammonium oxalate than in water and often fails to form due to supersaturation. The reaction appears to have little value as a qualitative test for magnesium.[21,22]

Separation of the alkalies from the alkaline earths. If a chloride or nitrate solution is evaporated with an excess of oxalic acid and the residue then heated until the excess is expelled, the alkaline earths are converted into insoluble carbonates and the alkalies into soluble carbonates.[23] To separate the alkaline earths from magnesia, the oxalate residue is ignited to obtain oxides, from which the alkaline earths may be extracted with carbon dioxide-free water. Zinc, copper and manganese are dissolved from a mixture with iron and aluminum by extracting the ignited oxalate residue with dilute hydrochloric acid.

Detection and determination of beryllium. The formation of beryllium oxalate crystals constitutes a very satisfactory method for the microchemical detection of beryllium.[21,24] By the use of potassium oxalate 0.08γ of beryllium can be detected.

Beryllium forms a slightly dissociated compound with the oxalate ion in which the ratio of beryllium to oxalate is 1:1. This makes possible the conductometric titration of beryllium.[25] This method is said to give results accurate to 5 per cent with 0.9-1.2 mg. of beryllium, and an accuracy of 10 per cent with 0.4 mg. of beryllium. Aluminum interferes with this method.

Detection of sodium. Sodium oxalate is much less soluble in water and dilute alcohol than are the corresponding potassium and ammonium salts. This makes possible the detection of sodium in the presence of potassium and ammonium. Winkler [26] recommends making the test by adding a saturated solution of potassium oxalate and a little alcohol. Meyerfeld [27] has used a saturated solution of ammonium oxalate, while Schoorl [28] makes the test by shaking 0.5 g. of the solid to be tested for sodium with 2.5 ml. of a 20 per cent potassium oxalate solution.

Determination of aluminum. Oxalic acid and its salts do not yield precipitates in solutions of aluminum salts. This characteristic makes possible the differentiation of aluminum from cerium, lanthanum, praseodymium, neodymium, erbium and the alkaline earths.

Wohlk [29] has determined aluminum titrimetrically in a procedure which is based upon precipitation of aluminum as the hydroxide, solution of the precipitate in a measured volume of hot N oxalic acid solution, and titration of excess acid with N sodium hydroxide.

Procedure. To a solution of the aluminum salt, add ammonium chloride and ammonium hydroxide dropwise until the mixture is basic to methyl red. Heat to boiling, allow the aluminum hydroxide to settle, and filter. Dissolve the precipitate in acid and repeat the precipitation. Dissolve the washed precipitate in a measured volume of hot N oxalic acid and titrate the excess acid with N sodium hydroxide using methyl red as indicator.

Determination of zinc and cadmium. Zinc may be determined in the absence of interfering ions by precipitating as zinc oxalate and igniting to the oxide.[30-33] The following procedure may be used for the determination of zinc in brass.

Procedure. Dissolve 0.3 g. of brass in nitric and sulfuric acids and remove the copper electrolytically. Neutralize with sodium hydroxide to methyl orange, acidify with 3 drops of sulfuric acid and concentrate to 40 ml. Add 0.5 g.

of oxalic acid dissolved in 10 ml. of water and heat to boiling, and then allow to stand for 18 hours. Filter the zinc oxalate precipitate, wash with a minimum of cold water, dry with alcohol and ether and heat to redness in a current of air. Weigh as ZnO.

Oxalic acid is also used in the electrolytic determination of zinc. A rapid deposition of zinc may be obtained from a zinc salt solution containing ammonium oxalate and free oxalic acid.[34,35] Zinc may also be separated from manganese by separating the zinc from a solution containing free oxalic acid, which prevents the formation of manganese dioxide upon the anode.[34,35] Zinc may also be separated from cadmium by the electrolysis of a potassium oxalate-ammonium oxalate solution.[36,37]

Cadmium is deposited in compact form and with a bright metallic luster by the electrolysis of a solution of complex ammonium cadmium oxalate in the presence of free oxalic acid. The solution should be heated to 70-75° C.[38,39]

Determination of lead. Lead may be determined by precipitating as lead oxalate. The solution of lead salt is first neutralized with ammonia, and a sufficient quantity of acetic acid is added to make the solution about 0.5 N. Lead is then precipitated with oxalic acid at room temperature. Lead is determined by titrating the acid solution of the oxalate with potassium permanganate.[40] Kolhoff [41] has suggested titrating lead conductometrically with a N solution of lithium oxalate.

Determination of copper and silver. Silver and copper may be titrated conductometrically with a N solution of lithium oxalate.[41]

Determination of nickel, iron and cobalt. Nickel and cobalt may be precipitated as the corresponding oxalates, which may be ignited and weighed as the oxides or determined titrimetrically after dissolving in dilute acid.[31-33,42]

DeGray and Ritterhausen [43] have proposed a method for the separation of iron from cobalt or nickel with the aid of oxalic acid. When ammonium hydroxide is added slowly to a solution of cobalt sulfate, insoluble cobalt hydroxide forms. This dissolves in an excess of the precipitant. If this solution is boiled, cobalt hydroxide is reprecipitated. Thus if ferric hydroxide is precipitated by ammonium hydroxide in the presence of cobalt, the precipitate may be contaminated by small quantities of cobalt. If oxalates are present, however, cobalt does not at any time yield a precipitate upon the slow addition of ammonium hydroxide, and even after prolonged boiling precipitation does not occur. Nickel behaves in a similar manner.

The following method may be used for the separation of iron from cobalt:

Procedure. The sample to be analyzed should contain from 0.5 to 4 mg. of cobalt. If the ratio of iron to cobalt is greater than 10:1, the chloride solution should be extracted with ether until the ratio is reduced to 10:1.

Make the solution containing cobalt and iron slightly acid and dilute to 200 ml. Add 10 ml. of 10 per cent oxalic acid solution, then neutralize with ammonium hydroxide and add 5 ml. in excess. Boil to coagulate the precipitate, filter, and wash. Cobalt is in the filtrate while iron remains on the filter.

A solution containing iron and nickel in a ratio not to exceed 10:1 may be separated in the same manner. Oxalic acid does not interfere with the colorimetric determination of cobalt by the Vogel reaction nor with the determination of nickel as nickel dimethylglyoxime.

Cartledge and Nichols[44] have proposed a new spectrophotometric method for determining cobalt which is much more rapid than the older gravimetric or electrolytic procedures. The basis for this procedure is the measurement of the absorption at 605 mμ caused by the trioxalatocobaltiate ion, $[Co(C_2O_4)_3]^{-3}$, which is formed by the oxidation of a solution of a cobaltous salt by lead dioxide in a slightly acid solution of potassium oxalate.[45] This reaction is given by the following equation:

$$2CoSO_4 + 4HC_2H_3O_2 + 7K_2C_2O_4 + PbO_2 \rightarrow 2K_3Co(C_2O_4)_3 + PbC_2O_4 + 4KC_2H_3O_2 + 2K_2SO_4 + 2H_2O$$

The trioxalatocobaltiate ion has a dark emerald-green color with a maximum absorption at 605 mμ.[46] This method is said to be accurate to about 2 per cent.

Procedure. Treat an aliquot containing 1-50 mg. of cobalt with sodium hydroxide until a slightly permanent precipitate is formed. The volume of the solution at this point should not exceed 25 ml. Next add 2 ml. of glacial acetic acid, 5 ml. of 20 per cent ammonium acetate, 10 ml. of 1 M potassium oxalate and 1 g. of manganese-free lead dioxide. Allow the mixture to stand at room temperature for 5-10 minutes in a place sheltered from bright light. The solution should be shaken from time to time. After 10 minutes (not longer) dilute to either 50 or 100 ml., depending upon the cobalt concentration. Immediately after dilution, filter through a Whatman No. 42 and discard the first portion of the filtrate. Then cool a sufficient volume in the absorption cell and measure in a spectrophotometer.

It is important that the solution be clear. If a second filtration is needed, add a little more lead dioxide. The length of the cell used for the measurements should be 1 to 5 cm.

The results obtained by the above method are given in Table 8.

TABLE 8.—DETERMINATION OF COBALT

Cobalt Present mg.	Volume ml.	Cell Length cm.	Cobalt Found mg.	Error mg.
1.56	50	4	1.59	+0.03
3.89	50	4	3.86	—0.03
7.78	100	4	7.80	+0.02
11.75	100	3	11.82	+0.07
11.75	100	3	11.64	—0.11
11.94	100	3	11.97	+0.03
15.56	100	2	15.5	—0.1
29.5	100	1	29.65	+0.15
31.1	100	1	30.8	—0.3
41.45	100	1	41.1	—0.35

Trivalent chromium interferes in this determination but may be oxidized to the weakly absorbing dichromate by preliminary treatment with lead dioxide and nitric acid. Copper and manganese interfere and must be removed.

It is very difficult to deposit iron, cobalt and nickel quantitatively by electrolysis unless the hydrogen-ion concentration of the solution is kept quite low. This may be accomplished by the use of a small quantity of oxalic acid in the presence of a large excess of an alkali oxalate.[47] The metals are usually deposited from an alkaline solution. When a cold solution containing iron and aluminum and a large excess of ammonium oxalate is electrolyzed, iron is deposited on the cathode while aluminum remains in solution. Iron may be separated from beryllium by a similar procedure.[48]

Determination of uranium and the rare earths. The separation of uranium from rare earths by precipitating with an alkali oxalate is not satisfactory. Some uranium is coprecipitated, and the rare earths are only incompletely precipitated in the presence of uranyl salts.[49-51]

Detection and determination of manganese. When acetic acid is added to a solution containing manganese and an excess of potassium oxalate, the potassium manganese oxalate is decomposed and manganous oxalate is formed. This compound is completely insoluble in acetic acid. A double oxalate is also formed with ferric iron, but this compound is not decomposed by the acetic acid treatment. Thus, manganese may be precipitated in the presence of iron.[32,33]

Hermans [54] and Caron and Raquet [55,56] reported independently a method for the detection of manganese which is based upon the use of an alkali oxalate. Solutions of manganous salts when treated with an alkali oxalate and certain oxidizing agents, such as dichromate, hypochlorite and sodium peroxide, in an acid medium yield an intense currant-red color due to the formation of a double oxalate. Mineral acids in excess cause the disappearance of the color, but the test can be made in a free mineral acid solution by the addition of sodium acetate or an excess of potassium oxalate. This test is less sensitive than that based on the formation of the permanganate ion, but possesses the advantage of being used in the presence of chlorides. The test originally proposed by Caron and Raquet [55] is performed as follows:

Procedure. To 10 ml. of the manganese solution add 2 ml. of saturated potassium oxalate solution, 1 ml. of glacial acetic acid and a few drops of potassium hypochlorite solution. A red color is obtained with as little as 1 part of manganese in 20,000 parts of solution.

Zinc does not interfere with the above test but iron salts must be absent.[56]

Deniges [57] states that the reaction can be performed without the use of acetic acid and hypochlorite by shaking the alkaline solution with air.

Procedure. Two drops of sodium hydroxide solution are added to 5 ml. of the manganese solution and the contents are shaken with air until the precipitate is quite brown. Then add dropwise a cold saturated solution of oxalic acid until the brown tint disappears. A currant-red coloration appears with manganese.

A modification of the Caron and Raquet test [55,56] for manganese has been used by Macri [58] and Sacher.[59] The latter test is performed as follows:

Procedure. To a solution of the material to be tested,, prepared with the aid of acid if necessary, add sodium hydroxide, and warm. Cool and add dropwise 0.5 N oxalic acid. A red color is obtained with 1 part of manganese in 200,000 parts of solution.

This test has been applied to the detection of manganese in lacquers and dryers.

Wenger and Duckert [60] do not recommend the method of Sacher since a similar reaction is given by other ions of the same group.

Wester [61] has studied the possibility of using the reaction of manganese with oxalate for the colorimetric determination of manganese, but has reported that this method is unsatisfactory.

Detection of nitrite. Hermans,[54] in a test similar to that proposed by Caron and Raquet,[55,56] observed that a solution of manganous sulfate and potassium oxalate acidified with acetic acid turns rose-red upon the addition of a few drops of sodium nitrite solution. This reaction has been used as a test for nitrites and for manganese. The following procedure may be used for the detection of nitrite in the presence of nitrate.[62]

Procedure. Add a few drops of glacial acetic acid to 2 ml. of the solution to be tested, and add 2 ml. of 5 per cent potassium oxalate solution, 1 ml. of 5 per cent manganous sulfate solution and a few drops of 3 per cent hydrogen peroxide. Lead peroxide can be used. A red color is obtained with as little as 0.02 g. of sodium nitrite per liter of solution.

Hahn [63] has used oxalic acid in the preparation of a reagent for detecting nitrite with the aid of *α*-naphthylamine and sulfanilic acid. The directions for preparing the reagent and carrying out the test are given in the section on *α*-naphthylamine (page 404). Salei [64] has used oxalic acid in preparing a dry reagent with *α*-naphthylamine and sulfanilic acid (page 404).

Detection and determination of cerium. When oxalic acid is added to a concentrated solution of a ceric salt, a dirty orange precipitate forms which gradually becomes yellow and gelatinous if more oxalic acid is added. The precipitate dissolves in a large excess of oxalic acid but the solution gradually becomes turbid on standing, or more quickly on heating, due to reduction of ceric to cerous salt. Eventually all cerium is precipitated as cerous oxalate. This reaction is different from that of lanthanum, praseodymium, neodymium and the yttrium earths, and may be used for the detection of cerium.[65] When dilute cerium solutions are precipitated with oxalic acid or ammonium oxalate, the curdy white precipitate becomes crystalline and may be used for the microchemical detection of cerium.[67] Wenger and co-workers [66] do not recommend oxalic acid as a reagent for cerium since oxalic acid yields precipitates with too many metals. Brinton and James [68] recommend precipitating cerium as ceric iodate and eventually converting to cerium oxalate by boiling with oxalic acid. The procedure is essentially the same as that employed with thorium (see below). Satisfactory results are claimed in determining cerium by this method.

Detection of yttrium. When a drop of a concentrated solution of oxalic acid is placed in contact with a drop of a dilute solution of yttrium sulfate, a crystalline precipitate is obtained which may be used for the detection of yttrium.

Detection of lanthanum. Oxalic acid produces, with lanthanum salts, a white crystalline precipitate which is insoluble in an excess of the acid and in ammonium oxalate, but which is soluble in dilute mineral acids. This reaction may be used to differentiate between lanthanum and thorium.[69]

Detection and determination of thorium. Thorium is quantitatively precipitated from solutions which are not too strongly acid by the addition of oxalic acid. The crystalline oxalate is practically insoluble in oxalic acid and in dilute mineral acids. The oxalate dissolves in ammonium acetate solutions containing a little free acetic acid. On boiling it dissolves in concentrated alkali oxalate solutions and in ammonium oxalate to form very stable complex ions, $[Th(C_2O_4)_4]^{-4}$, $[Th(C_2O_4)_3]^{-2}$, or $[Th_2(C_2O_4)_5]^{-2}$. No precipitate separates when the complex ion is formed if sufficient ammonium oxalate is present. This behavior is different from that of cerium, lanthanum, praseodymium, neodymium and somewhat different from yttrium and erbium. Upon adding hydrochloric acid, the complex oxalate ion is decomposed and thorium oxalate is precipitated.

Thorium is precipitated by ammonium oxalate, and the precipitate redissolves on boiling with an excess of the precipitant. The solution remains clear on cooling provided sufficient ammonium oxalate is present and the original solution was not too strongly acid. Thorium is precipitated from the boiling complex oxalate solution by the addition of hydrochloric acid. This behavior is unlike that of zirconium.

Oxalic acid or ammonium oxalate may be used for the detection of thorium,[67,70,71] but Wenger and Duckert [72] do not recommend it since other reagents are said to give better results.

Since thorium is quantitatively precipitated by oxalic acid, this reagent has been used for the determination of thorium.[73-75]. Kaufman [76] recommends a procedure which combines two methods: The precipitation of thorium with potassium iodate according to the method of Meyer [77] and the conversion of the iodate to the oxalate by the method of Brinton and James.[78] The advantages claimed for this method are that no separation of the rare earths from the third group is necessary; the reaction may be carried out in a strongly acid solution; and small amounts of thorium can be determined in minerals containing titanium, zirconium and scandium.

Reagents. *Reagent A:* Dissolve 15 g. of potassium iodate and 50 ml. of nitric acid ($d = 1.4$) in 100 ml. of water.

Reagent B: Dissolve 8 g. of potassium iodate and 200 ml. of nitric acid ($d = 1.2$) in 800 ml. of water.

Procedure. To 10-40 ml. of a thorium solution containing 25 per cent nitric acid, and which may contain a large excess of cerium, add an equal volume of reagent A and digest at 60-80° C. for 15 minutes. Then add 2 volumes of reagent B and filter while cold through a dense filter paper. Transfer the filtrate and precipitate to the same beaker, stir well, again filter and wash the precipitate free of cerium with reagent B. For solutions containing not more than 10-20 mg. of thorium and 0.1-0.2 g. of cerium, one precipitation is sufficient. With concentrated solutions, or in the presence of large quantities of iron, aluminum and uranium, transfer the precipitate to the original beaker with a little hot water and dissolve by heating and adding nitric acid dropwise. Evaporate or dilute as necessary until the concentration of nitric acid is 25 per cent and again precipitate and wash as described above.

Transfer the precipitate with the filter to the original beaker and add 2-3 g. of crystalline oxalic acid and 50 ml. of water. Heat carefully at first and finally boil until the iodate is decomposed and iodine is expelled. Dilute with water, filter, wash and ignite to thorium oxide.

Determination of tin. Tin may be determined electrolytically by depositing from an acid oxalate solution.[79] An excess of oxalic acid must be present in the ammonium oxalate solution until all tin has been deposited, since otherwise the solution gradually becomes alkaline due to the oxidation of ammonium oxalate at the anode. Stannic acid separates from the solution as it becomes alkaline. In the presence of an excess of oxalic acid, tin is deposited upon the cathode in a bright metallic form.

Wheeler [80] observed that stannic tin in an oxalic acid solution forms a fairly stable compound with sulfur upon treatment with hydrogen sulfide. Using this principle Wheeler [80] proposed a titrimetric method for determining tin in bronze by titrating the sulfur with iodine. According to Willard and Toribara [81] this method is unsatisfactory since conditions must be very carefully adjusted in order to obtain the theoretical relationship between tin and sulfur. Accordingly, these authors have proposed a new method which is based on the following steps: A solution of stannic tin is converted to potassium oxalatostannate, $K_6Sn_2(C_2O_4)_7$, by adding potassium oxalate until the solution has a definite acidity. A pH range of 2.2-2.8 is satisfactory if potassium sulfide is subsequently used, or approximately 3.3 if hydrogen sulfide gas is used. The salt is then converted to dipotassium dioxalatothiometastannate, $K_2SnS(C_2O_4)_2$, by the addition of potassium sulfide or hydrogen sulfide. The excess hydrogen sulfide is removed by a current of carbon dioxide, and the sulfur in the complex is then titrated with a standard iodine solution.

The reactions involved in the method proposed by Willard and Toribara [81] are shown by the following equations:

$$K_6Sn_2(C_2O_4)_7 + 2H_2S \rightarrow 2K_2SnS(C_2O_4)_2 + 2H_2C_2O_4 + K_2C_2O_4$$

$$2K_2SnS(C_2O_4)_2 + 2I_2 + 2H_2C_2O_4 + K_2C_2O_4 \rightarrow K_6Sn_2(C_2O_4)_7 + 4HI + 2S$$

A sample containing pure tin may be determined as follows:

Reagent. *Potassium sulfide solution:* Dissolve 20 g. of potassium hydroxide in 100 ml. of water and saturate with hydrogen sulfide. Keep the solution cold while adding hydrogen sulfide. Keep this solution in an atmosphere of carbon dioxide.

Wash liquid. Dissolve 5 g. of oxalic acid in 1 liter of water and add potassium oxalate until the solution has a pH of 3.

Procedure. Dissolve about 0.15 g. of tin in 2 ml. of concentrated sulfuric acid and several ml. of concentrated nitric acid. Evaporate until fumes of sulfur trioxide appear and cool the mixture. Add 2-3 g. of solid potassium oxalate and wash down the sides of the beaker and the cover glass with about 20 ml. of the wash liquid. Add solid potassium oxalate until the pH is 2.2-2.8. This is determined by using thymol blue, and adding potassium oxalate until all the red tint disappears. A glass electrode may also be used.

Dilute the solution to 60 ml. and heat to 60° C. Add dropwise and with mechanical stirring 3.5 ml. of potassium sulfide solution. The beaker should be covered with a split watch glass since considerable gas is evolved. Heat for 5 minutes at 60° C. and add a few more drops of the potassium sulfide solution, and heat for an additional minute. Cool to room temperature in a stream of cold water. Stir mechanically and pass carbon dioxide through the mixture until the escaping gas yields no test for hydrogen sulfide with lead acetate paper. Finally titrate the solution with 0.1 N iodine solution to a faint yellow color. This is about 1 ml. beyond the end-point. Finally add starch solution and back titrate with standard thiosulfate. One ml. of 0.1 N iodine is equivalent to 0.005935 g. of tin.

This method yields excellent results with pure tin, but with alloys interfering substances must be removed. The method may, however, be applied with suitable modifications to the analysis of certain alloys. In the presence of considerable quantities of other metals, tin is first separated as metastannic acid.

Separation of titanium from tantalum and columbium. Schoeller and co-workers[82-85] have studied various methods for the separation of titanium from tantalum and columbium, and report that the oxalate-salicylate method gives excellent results. The oxalate-salicylate method is based upon the following principle: when a solution containing ammonium and titanium oxalates and a small quantity of the oxalo-earth acids is treated with an excess of sodium salicylate, the characteristic orange color of the salicylic-titanium complex is formed. If the oxalic acid is removed with calcium chloride, the bulky precipitate of calcium oxalate carries down the earth acids while the titanium complex remains in solution. Precipitation is not quantitative, so titanium must be recovered from the filtrate and the treatment repeated. The oxalate precipitates are dissolved in hydrochloric acid and oxalic acid destroyed with potassium permanganate. The earth acids are precipitated from the acid solution as the tannin complex. The ignited precipitates are then submitted to tartaric hydrolysis (page 182). The complete saparation involves a number of steps, since retreatment of the various fractions is necessary, but the preliminary separation may be carried out as follows:

Procedure. Fuse approximately 0.25 g. of the mixed oxides with 3 g. of potassium bisulfate in a silica crucible and treat the mass with a hot concentrated solution containing 2 g. of ammonium oxalate. Dissolve 5 g. of sodium salicylate in hot water and add with constant stirring to the boiling solution, which should have a volume of about 250 ml. Precipitate the solution with a slight excess of 20 per cent calcium chloride solution added gradually and in small portions. Do not allow the mixture to become cool. Allow to settle on a water-bath and test the supernatant liquid for complete precipitation with a little calcium chloride. Filter immediately with suction on a 11 cm. Whatman No. 40 filter paper supported on a platinum cone. Wash the precipitate with hot 2 per cent sodium salicylate until the washings are colorless. The major portion of the earth acids is in the oxalate precipitate while titanium is in the filtrate.

Separation of tantalum and columbium. Wirtz[152] recommends the use of ammonium oxalate for the separation of tantalum and columbium. Tantalum does not precipitate until an acidity of pH 2.4 is reached, but columbium precipitates appreciably at pH 1.9.

Determination of gold. Gold is precipitated quantitatively by boiling with oxalic acid.[86]

Detection and determination of chromium. If a drop of one per cent chromic chloride solution is treated with a drop of a concentrated solution of oxalic acid and a drop of quinoline solution on a microscope slide, crystals of $[Cr(C_2O_4)_2]C_9H_7N$ are obtained. Martini[87] has used this reaction for the microchemical detection of chromium. The test is said to be sensitive to 0.01 mg. of chromium.

By boiling solutions of chromic salts or chromates with oxalic acid, trioxalatochromic complexes are formed. About 10 moles of oxalic acid are necessary for each mole of chromium. The chromium complex has an intense blue-violet color and obeys the Lambert-Beer Law. The extinction curve has a maximum of about 570 mμ. The concentration of chromium can be measured accurately with a step photometer or less accurately by comparing with standard solutions of known chromium content. Ueberbacher and Droscher[88] have used this principle for the determination of chromium in leather.

Separation of antimony and tin. Antimony is completely precipitated by hydrogen sulfide from a solution containing oxalic acid while stannic tin is not. This difference in the behavior of antimony and tin provides one of the most satisfactory methods for the separation of these metals. Stannous sulfide is decomposed by oxalic acid to form an insoluble crystalline stannous oxalate, and so tin must be present in the stannic condition.[89-93]

Separation of titanium and aluminum. Titanium can be separated from aluminum in an oxalic acid solution at a pH of 5.6-6.5 with the aid of 8-hydroxyquinoline.[94]

Detection of the platinum metals. Whitmore and Schneider[95] have investigated the use of ammonium oxalate as a microchemical reagent for the detection of metals of the platinum group. The results obtained on adding a fragment of ammonium oxalate to a 2 per cent solution of the metal salts is given in Table 9.

TABLE 9.—DETECTION OF THE PLATINUM METALS

Test Material	Description
$RuCl_3$	No apparent reaction
$RhCl_3$	No apparent reaction
$PdCl_2$	Long slender, bright-yellow prisms appear very gradually around the test particle, and also around edge of drop.
Na_2OsCl_6	Many garnet-red octahedra appear gradually, first around the edge and then over entire drop.
$IrCl_4$	Many deep purple octahedra develop immediately.
H_2PtCl_6	A great many, bright-yellow octahedra appear immediately.
$AuCl_3$	A blue amorphous precipitate forms around the test particle immediately.

Detection of bromate. Hahn[96] has used oxalic acid with fluorescein in testing for bromates.

Oxalic acid as a titrimetric standard. In 1852 Mohr recommended well-crystallized oxalic acid for the standardization of solutions of alkalies, permanganates and thiosulfates.[97-100] Oxalic acid is obtained as the dihydrate, $H_2C_2O_4 \cdot 2H_2O$, and has an equivalent weight of 63.02. Various authors have stated that it is difficult to obtain the acid free from salts and containing exactly two moles of water.[101-103] To eliminate this difficulty Hampe,[104,105] Lehfeldt[106] and Winkler[107] studied the use of anhydrous oxalic acid sublimed at 100° C. Treadwell and Johner[108] dehydrated pure recrystallized oxalic acid, first at 100° C., and then by sublimation at 140° C. under reduced pressure. The sublimate should quickly be placed in a tightly covered weighing bottle and heated to 100° C. in a drying oven and then cooled in a vacuum desiccator over calcium chloride.[104,105] The use of the anhydrous acid has not been very satisfactory, however, since it is very hygroscopic. Kolthoff[109] advises against the use of the anhydrous compound as a primary standard.

Commercial oxalic acid can be purified for use as a standard according to the method of Winkler.[107]

Procedure. Dissolve 500 g. of commercial acid in 500 ml. of boiling 14 per cent hydrochloric acid ($d = 1.07$) and allow to cool while stirring. Filter through a funnel containing glass wool and allow to drain. Cover several times with hydrochloric acid while in the funnel, and then dissolve the solid in pure boiling hydrochloric acid. Again cool with stirring, wash and dissolve in the least possible quantity of water. The oxalic acid that crystallizes on cooling is washed and recrystallized from water until free of chloride ion. Dry to constant weight in the presence of anhydrous calcium chloride.

It is difficult to obtain crystallized oxalic acid that is free from occluded and adsorbed water. According to Hill and Smith,[110] large crystals may inclose several tenths of a per cent of water. A product corresponding in composition to exactly $H_2C_2O_4 \cdot 2H_2O$ may be obtained by powdering the crystals and drying over a mixture of the crystallized and anhydrous acid. Hill and Smith[110] recommend passing a stream of air over the powdered crystals after first passing through a large bottle filled with a mixture of anhydrous and hydrated oxalic acid. Treadwell [108] recommends the same procedure.

Schoorl [111] claims that vacuole water is completely removed by dehydrating the hydrated acid at 60° C. in a desiccator and then allowing the acid to absorb water by standing in air or in a desiccator over deliquescent sodium bromide.

Since the second dissociation constant of oxalic acid is relatively small, it cannot be titrated accurately with alkali-sensitive indicators like methyl yellow or methyl orange, but satsfactory results are obtained with phenolphthalein or thymol blue. Water used in the titration must be free from carbonic acid because of the sensitivity of the indicators to this compound. In standardizing the base, the weighed quantity of oxalic acid is dissolved in water and titrated with the alkali solution to the appearance of a pink color with phenolphthalein.

Bruhns [112-115] has found that oxalic acid reacts as a stronger acid in the presence of the calcium salt of a strong acid. In the reaction:

$$H_2C_2O_4 + CaCl_2 \rightarrow CaC_2O_4 + 2HCl$$

the quantity of hydrochloric acid set free is equivalent to the amount of oxalic acid used. According to Schmitt [116] the oxalate solution should be practically neutral before the calcium chloride is added, and this view is confirmed by Kolthoff.[109] The calcium solution is not added until the acid has been almost completely neutralized. Under these conditions a sharp end-point is obtained with methyl yellow. According to Kolthoff [109] and Ishimaru [117] the titer of a 0.1 N solution of oxalic acid does not change if stored in a dark bottle and protected from light. More dilute solutions are less stable.

Oxalic acid may also be used for the standardization of solutions of potassium permanganate, although there are several possible sources of error.[118]. These include oxidation of oxalic acid by oxygen of air; decomposition of oxalic acid into carbon dioxide and water; loss of oxygen; purity of water and acid; formation of abnormal oxidation products; and the presence of hydrochloric acid.[119,120] Consequently in the titration of oxalic acid, and in the standardization of permanganate against oxalic acid, accurate results may be obtained only by strictly adhering to the following conditions:[109] Dissolve an exactly weighed quantity of oxalic acid in sufficient water to make its concentration approximately 0.1 N and then add 15 ml. of 4 N sulfuric acid for each 50 ml. of solution. Heat the mixture to 75-80° C. and titrate with the permanaganate solution. Add the permanganate slowly, particularly at the beginning of the titration, and wait each time until the solution becomes colorless. Then continue the titration to the end-point with continuous stirring. Excellent results are obtained when this method is followed Oxalic acid is said to be superior to adipic acid for standardizing potassium permanganate solutions.[121]

Oxalic acid has also been used for the standardization of sodium thiosulfate solutions. The fundamental reaction involved occurs between the hydrogen ion, iodide and iodate to form free iodine:

$$6H^+ + 5I^- + IO_3^- \rightarrow 3H_2O + 3I_2$$

If a calcium or magnesium salt of a stronger acid is added, the oxalate ions are precipitated or transformed into a complex and an equivalent quantity of acid is set free. In this way the reaction may be made to run quantitatively to completion.

Procedure. Dissolve an accurately weighed sample of oxalic acid in water and to each 50 ml. of 0.1 N oxalic acid solution add 12.5 ml. of 0.1 M magnesium chloride, 10 ml. of N potassium iodide and 10 ml. of 3 per cent potassium iodate. Titrate this mixture with the thiosulfate solution, adding starch toward the end of the determination.

Sodium oxalate as a titrimetric standard. Sorensen[122-126] has recommended sodium oxalate, equivalent weight 66.98, as an excellent primary standard for the standardization of acids and permanganates.[127] The salt may be obtained free of water of hydration and it is not hygroscopic. The commercial salt may be purified according to the method of Sorensen.

Procedure. Dissolve commercial sodium oxalate in a little water, make slightly alkaline and allow to stand until completely clear. Filter and evaporate the filtrate to one-tenth of its original volume. Sodium oxalate separates from the solution in a crystalline condition, while most soluble impurities remain in solution. Filter, pulverize the salt, and wash several times with water. Repeat the above treatment until the filtrate is clear and free of sulfuric acid, and is practically neutral to phenolphthalein.

Better results are obtained by using sodium oxalate that has been precipitated from a warm saturated solution with alcohol. The salt is filtered and dried at 240° C. Schoorl states that precipitation with alcohol is not necessary if the salt is dried at 240° C. before converting to the carbonate.

Sodium oxalate is converted to sodium carbonate by carefully heating the salt. Sorensen recommends heating an accurately weighed quantity of the oxalate in a platinum crucible fitted with an inclined lid. The heating period is 15-30 minutes, and a small gas flame is used. Lunge[128,129] states that gas which may contain sulfur dioxide should not be allowed to come in contact with the contents of the crucible. The crucible is covered and heated for 15 minutes over a very small flame, and then more strongly with access of air until the sodium carbonate begins to melt. A part of the sodium carbonate is decomposed to sodium oxide by this treatment, but this does not interfere with the titration by the acid. The material must not be heated too strongly since some sodium oxide may be lost by volatilization. To complete the standardization of the acid, proceed as follows:[109]

Procedure. After cooling the ignited sodium oxalate add a little water to the platinum crucible and place the crucible in an upright position in a beaker containing an excess of the acid to be standardized. No acid should be permitted to enter the crucible. After the contents of the crucible are thoroughly moistened, cover the beaker with a watch glass and tilt the beaker so that the acid enters the crucible. Heat on a water-bath until carbon dioxide is expelled and transfer the liquid to an Erlenmeyer flask. Wash the beaker, crucible and lid carefully with water. Add a few drops of phenolphthalein, boil to remove all carbon dioxide, cool with cold water, and titrate the excess acid with standardized sodium hydroxide solution.

Lunge [129] recommends the direct titration of the carbonate using methyl orange as an indicator. Kuster [130] suggested a modification of the direct titration method to avoid errors arising from the presence of carbon dioxide and sodium chloride.

Sodium oxalate may be used for standardizing permanganate solutions.[118,131,132] This method is claimed to be the most reliable of all of those that have been proposed. McBride [118] recommends the following procedure for the standardization.

Procedure. In a 300-ml. beaker, dissolve 0.25-0.3 g. of sodium oxalate (dried for 1 hour at 130° C.) in 200-250 ml. of water heated to 80-90° C., and add 10 ml. of 1:1 sulfuric acid. Immediately titrate with 0.1 N potassium permanganate with vigorous and continuous stirring. Add the permanganate solution at a rate not exceeding 10-15 ml. per minute, and add the last 0.5-1.0 ml. dropwise. During the dropwise addition, the solution should become fully decolorized before adding another drop. The excess permanganate required to show a color at the end-point must be estimated by matching the color in a second beaker containing the same volume of acid in hot water. The temperature of the solution should not fall below 60° C. The calculation is based upon the following equation:

$$2KMnO_4 + 5Na_2C_2O_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5Na_2SO_4 + 10CO_2 + 8H_2O$$

One thousand ml. of 0.1 N permanganate solution reacts with exactly 6.700 g. of sodium oxalate. Sodium oxalate has also been used as a standard in cerate oxidimetry.[133]

The oxalate ion may be used as a catalyst in the reaction for standardizing iodometric solutions against potassium dichromate so that less hydrochloric acid is required. In this way more accurate results are obtained, since hydrochloric acid causes an error due to the auto-oxidation of hydrogen iodide by atmospheric oxygen.[134]

Potassium acid oxalate as a titrimetric standard. Osaka and Ando [135,136] have suggested the use of potassium acid oxalate for the standardization of alkali solutions. It possesses the advantage of crystallizing without water of hydration, but the salt cannot be crystallized conveniently, since at a temperature below 40° C. a salt having a different composition separates from the saturated solution. For the preparation of the compound, Kolthoff[109] recommends the following procedure:

Procedure. Mix equal molecular quantities of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) and potassium oxalate ($K_2C_2O_4 \cdot H_2O$) and recrystallize from water. During the recrystallization, 8 g. of oxalic acid and 16 g. of potassium oxalate must be present for each 100 g. of water. The mixture is dissolved by heating, and the anhydrous potassium acid oxalate is crystallized out between 15° and 60° C. The crystals are washed 3 or 4 times with water at 50° C. and are then thoroughly tested for impurities, particularly occluded water. The equivalent weight as an acid is 128.12.

Potassium tetroxalate as an alkalimetric standard. Potassium tetroxalate, $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$, is a double salt of oxalic acid and potassium acid oxalate. It crystallizes in colorless prisms that are soluble in water. The crystallized salt was first proposed as a standard by Kraut,[137-139] and has more recently been recommended by various investigators.[140-144] Others, however, report that the material is not suitable as a standard.[145-148] Wagner[149] and Kuhling[150,151] have described methods for preparing pure potassium tetroxalate, but according to Lunge[52] neither of these procedures yields a satisfactory product, since the water content is variable. Ulbricht and Meisel[142,143] have proposed a method, which is recommended by Schmitt,[53] by which a product of 99.94-99.98 per cent purity may be obtained:

Procedure. Dissolve 63 g. of pure oxalic acid in 100 ml. of distilled water with the aid of heat and similarly dissolve 30 g. of pure potassium oxalate in 100 ml. of water. Filter the two solutions while hot and mix while hot by adding the potassium oxalate solution to the oxalic acid solution while stirring continuously and cooling by immersing the vessel in ice water. Collect the crystals on a Buchner funnel, wash three times with water, and remove as much water as possible with suction. Transfer to a crystallizing dish and dry under reduced pressure to constant weight.

Calcium oxalate as a standard for permanganate solutions. Little and Beisler[15] recommend the use of calcium oxalate for the standardization of permanganate solutions.

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PALMITIC ACID

Synonym : Cetylic acid

$C_{16}H_{32}O_2$ Mol. Wt. 256.42 Beil Ref. II, 370

$CH_3(CH_2)_{14}CO_2H$

Use: Determination of barium, calcium, lead, magnesium (hardness of water), mercury, sulfate and zinc.

Palmitic acid is obtained from palm oil, Japan wax or Chinese vegetable tallow. It consists of white crystalline scales which melt at 61-62° C. It is insoluble in water, sparingly soluble in cold alcohol but freely soluble in hot alcohol, ether and chloroform.

Determination of calcium and magnesium (hardness of water). Palmitic acid has been substituted for stearic acid, oleic acid and mixed soaps for the determination of calcium and magnesium salts in water. Potassium palmitate, like other alkali soaps, is hydrolyzed in an aqueous solution. It also forms insoluble salts with the alkali earth metals. When potassium palmitate is added to a neutral solution of an alkaline earth salt the reaction becomes distinctly alkaline to phenolphthalein when all the metal is precipitated. This reaction of potassium palmitate has been used by Blacher and co-workers [1-3] for the determination of the hardness of water. It is reported by Kolthoff [4] to be especially satisfactory for this purpose, and also for the determination of barium, lead, zinc and mercury salts.

The reagent used for the titration may be prepared according to the method of Winkler.[5,6]

Potassium palmitate solution. Warm a mixture of 500 ml. of ethyl alcohol, 300 ml. of distilled water, 25.6 g. of purest palmitic acid and 0.1 g. of phenolphthalein. Warm the mixture on a water-bath and add clear alcoholic potassium hydroxide prepared by dissolving 7-8 g. of powdered potassium hydroxide in 50 ml. of hot 95 per cent alcohol until a faint red color appears, and then make the solution colorless with a drop of hydrochloric acid. Again treat with potassium hydroxide until a rose coloration results. After cooling, dilute the palmitate solution to 1 liter with 95 per cent alcohol. Below 15° C., palmitic acid gradually separates, and for this reason it is desirable to use propyl alcohol or neutral glycerol for the dilution instead of ethyl alcohol. A solution prepared in this manner is allowed to stand for several days and then filtered. It remains clear even on cooling to 0° C.

Standardization of potassium palmitate solution. Transfer to a 200-ml. bottle, approximately 40-50 ml. of clear lime water, which is prepared from ignited marble and pure carbon dioxide-free distilled water. Titrate the solution with 0.1 N hydrochloric acid to an end-point with 1 drop of 0.1 per cent methyl orange.

Dilute the neutralized solution with distilled water to 100 ml. and add 1 drop of bromine water. Then add 0.5 ml. of 1 per cent phenolphthalein and add 0.1 N sodium hydroxide dropwise until the solution is deep red, and the color does not fade on standing. Next add 0.1 N hydrochloric acid until the solution is just colorless, and finally add 1 drop in excess. Titrate this solution with potassium palmitate solution, with vigorous shaking, until the white solution (calcium palmitate), assumes a barely perceptible but distinct rose red color which remains for several minutes. Deduct 0.3 ml. from the volume of potassium palmitate solution used. If the titration is carried out to a barely perceptible rose color, deduct only 0.2 ml. If the potassium palmitate solution is properly prepared the corrected volume should be equal to that of the 0.1 N hydrochloric acid which was required for the original titration of the lime water.

Determination of hardness of water. Neutralize 100 ml. of water to methyl orange with 0.1 N hydrochloric acid (bicarbonate hardness). Expel the excess carbonic acid with a stream of air or by boiling the solution. Cool if the solution is boiled, and titrate with potassium palmitate as described in the procedure for standardization.

Weissenberger [7] and Kolthoff [8] report that magnesium salts require somewhat more potassium palmitate than do pure calcium solutions. According to Kolthoff,[8] in standardizing with magnesium salts the titer is about 2 per cent lower than when a calcium salt is used.

Iron interferes with the above procedure, but the interference may be eliminated by oxidizing with bromine water, treating with 10 ml. of 30 per cent Rochelle salt solution, then neutralizing to phenolphthalein and adding a drop of 0.1 N hydrochloric acid in excess.

According to Masters and Smith [9,10] the titration of calcium and magnesium with potassium palmitate is satisfactory at room temperature but is unreliable at 60° C. They also report unfavorably on the use of this reagent since a precipitate forms in the standard solution on standing for some time.

Determination of magnesium. Fromboese [11] has proposed a method for the determination of magnesium in the presence of calcium after converting calcium to the insoluble oxalate. This procedure has been modified by Kolthoff [12] as follows:

Procedure. Add 0.1 N hydrochloric acid to 200 ml. of water containing small quantities of calcium and magnesium until the solution is distinctly acid to methyl yellow. Heat to boiling and add dropwise 5 ml. of 10 per cent potassium oxalate solution. Cool, and neutralize to phenolphthalein, and then add 1 drop of 0.1 N hydrochloric acid in excess. Finally titrate with standard potassium palmitate solution to a permanent rose coloration and deduct 0.3 ml. from this volume.

Kolthoff [12] reports that this method gives excellent results with widely varying quantities of magnesium. It is necessary in carrying out this determination to re-standardize the potassium palmitate solution against pure magnesium sulfate.

Determination of barium and sulfate. Barium may be titrated in exactly the same manner as calcium with a standard potassium palmitate solution. This reaction may also be made the basis for an indirect determination of sulfate: [13]

Procedure. Make an exactly measured quantity of barium chloride solution slightly acid with 0.1 N hydrochloric acid, and add this to the boiling solution to be analyzed. Allow to stand for 10 minutes, then cool, neutralize to phenolphthalein, and add 1 drop of 0.1 N hydrochloric acid in excess. Titrate to a permanent rose-red color with standard potassium palmitate solution.

Results accurate to 1 per cent have been obtained with solutions containing as little as 100 mg. of sulfate per liter of solution, and results are still accurate to 4.4 per cent with solutions containing only 12 mg. of sulfate per liter.

Determination of lead. Lead is determined by titration with a palmitate solution in a manner similar to that employed for the estimation of the alkaline earth metals. A suitable 0.05 N solution is prepared by mixing 500 ml. of 0.1 N palmitic acid in propyl alcohol with 50 ml. of N sodium hydroxide in 96 per cent alcohol and diluting to 1 liter with 70 per cent propyl alcohol. A 0.2 per cent alcoholic solution of methyl yellow, an aqueous solution of α-naphthol orange or an aqueous solution of the sodium salt of methyl red can be used as an indicator. The lead solution must contain no impurities and must be neutral.[14]

Determination of zinc and mercury. Zinc and mercuric salts may be titrated with potassium palmitate in a manner similar to that with lead.

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PHTHALIC ACID

Synonym: *o*-Phthalic acid, benzenedicarboxylic acid

$C_8H_6O_4$ Mol. Wt. 166.13 Beil. Ref. IX, 791

$C_6H_4(CO_2H)_2$

Use: Alkalimetric standard.

Detection of cobalt, copper, germanium, mercury, nickel, potassium, strontium and zinc.
Determination of cobalt, iodate and lead.

Phthalic acid consists of colorless crystals which melt when rapidly heated at about 230° C., decomposing into a phthalic anhydride and water. Phthalic anhydride consists of white lustrous needles which melt at 130.8° C. It is soluble in 162 parts of water and dissolves more readily in hot water with the formation of phthalic acid. It is soluble in alcohol, but is only sparingly soluble in ether.

Use of phthalic acid as an alkalimetric standard. Many investigators[1-12] have recommended the use of potassium acid phthalate for the standardization of bases. This salt, $KHC_8H_4O_4$, is a colorless anhydrous crystalline compound. It is readily prepared by the half-neutralization of a solution of phthalic anhydride, and crystallizes readily in hexagonal plates, which may be dried at 120° C. This salt is stable, is not appreciably hygroscopic, and it may be weighed in an open container. One gram of the salt dissolves in 10-11 ml. of water at ordinary temperatures, and in about 400 g. of alcohol. Its equivalent weight, calculated from its use as an alkalimetric standard, is 204.22. This salt reacts with alkalies such as sodium hydroxide according to the following equation:

$$KHC_8H_4O_4 + NaOH \rightarrow KNaC_8H_4O_4 + H_2O$$

The neutrality of the alkali solution is calculated on the basis of this reaction.

Potassium acid phthalate of a high degree of purity may be obtained from the National Bureau of Standards, Washington, D. C. It is obtained as "Standard Sample 84," and is accompanied by a "Certificate of Analysis," which includes a statement of what is termed its "Effective Neutralizing Power." The certificate also contains full directions for its use as a standard in acidimetry.

The following directions for the standardization of 0.1 N sodium hydroxide solution are taken from the Bureau of Standards Certificate:

Procedure. Dry a few grams of the acid salt at 120° C. and cool in a desiccator containing a good dehydrating agent, and then weigh 1.000 g. of the dried salt into a 300-ml. flask which has been swept free of carbon dioxide. Add 50 ml. of cool, carbon dioxide-free water, and shake gently until solution is complete. Add 3 drops of a one per cent solution of phenolphthalein, and titrate with the 0.1 N sodium hydroxide solution, which is free of carbonate.

Determine the quantity of sodium hydroxide required to produce the end-point by matching with the color in another flask containing the same volume of water and indicator. The milli-equivalent of potassium acid phthalate is 0.2041.

For standardizing 0.5 N sodium hydroxide, use 3 g. of the salt. Unless special precautions are taken to exclude all carbon dioxide from the apparatus, and all carbonate from the solution of sodium hydroxide, too much of the sodium hydroxide solution will be used and the standardization will be low. To overcome the error due to the presence of carbonate, add sufficient standard acid to decolorize the solution and leave it slightly acid, heat the solution to boiling, boil gently for one minute, and add more acid if the color returns. Finally, cool and finish the titration with the base, making a correction for the volume of the acid used.

Sodium acid phthalate, $NaHC_8H_4O_4$, has also been proposed as an alkalimetric standard, but the potassium salt appears to be more satisfactory.[11-13] When sodium acid phthalate is crystallized from water at temperatures below 50° C., the crystalline product consists of the hemi-hydrate. When heated to 100-110° C., the crystals become anhydrous and opaque, but they retain their prismatic form.

Use of potassium acid phthalate as a pH standard. Recently the National Bureau of Standards has recommended the use of potassium acid phthalate as a pH sandard. The pH of a 0.05 M solution of the salt, calculated on the basis of its activity, is 4.008 at 25° C. At temperatures ranging from 0° to 60° C.

inclusive, the pH of the solution is given, within the limits of ±0.002 pH units, by the equation:

$$\mathrm{pH} = 5.13 \log T + 1519.67/T + 0.01092T - 17.039$$

where

$$T = t^\circ \mathrm{C.} + 273.16$$

The National Bureau of Standards recommends the following procedure for the preparation of a 0.05 M potassium acid phthalate solution:

Procedure. Crush lightly about 12 g. of pure potassium acid phthlate (N.B.S. Standard Sample 84a) to a fineness of approximately 100 mesh and dry for 1-2 hours at 120° C. Cool in a desiccator containing an effective dehydrating agent, such as magnesium perchlorate. Weigh out exactly 10.211 g. of the salt and add to 1000 g. of carbon dioxide-free distilled water (pH 6.7-7.3). A solution of the same concentration may also be prepared by adding 10.181 g. of the salt to 1 liter of water at 25° C., or 10.193 g. of the salt to 1 liter of water at 20° C.

Detection of potassium, cobalt, copper, mercury, strontium, zinc and nickel. Yorks and Willard [14] have studied the optical characteristics of the crystals of the phthalates of potassium, cobalt, copper, mercury, strontium, zinc and nickel with a view of using this information for the identification of these metals. Cobalt forms characteristic red crystals, copper blue crystals, and nickel green crystals.

Detection of germanium. Poluektov [15] has used phthalic acid for the preparation of hydroxynaphthacenequinonesulfonic acid, which is used as a reagent for a color reaction with germanium.

Determination of lead. Zombory [16] has found that lead is quantitatively precipitated as lead phthalate by means of an alkali phthalate in neutral solutions. At least 33 per cent of ethyl alcohol must be present to insure complete precipitation of the lead salt. It can be dried at 110° C. without decomposition and weighed. The precipitate contains 55.81 per cent lead. The alkalies and calcium and magnesium do not interfere with this determination but all other cations must be absent.

Determination of cobalt. Overholser and Yoe [19] recommend the use of phthalic acid as a buffer in the determination of cobalt with *o*-nitroresorcinol.

Determination of iodate in the presence of bromate and chlorate. Kolthoff and Hume [17] have found that it is possible to determine iodate by means of an ordinary iodometric titration without interference from chlorate or bromate if the reaction mixture is properly buffered with potassium hydrogen phthalate. After titration of the iodate, bromate can be titrated in the same reaction mixture by adding a suitable amount of hydrochloric acid and a few drops of a molybdate solution as a catalyst.[18]

The reaction between iodate and iodide is rapid and complete in solutions buffered with potassium acid phthalate between pH 4 and 5, but under the same conditions the reaction between bromate and iodide is slow. At pH 5 the oxidation of iodide by bromate is slow enough to be disregarded during the time required for the titration unless the bromate ion concentration is quite high. The potassium acid phthalate used in this determination serves to supply the hydrogen ions necessary for the reaction,

$$5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

and it also adjusts the acidity of the solution to the point where the iodate reaction is rapid, whereas the bromate reaction, although slow, is measurable. The pH of the mixture increases as the reaction between the iodide and the iodate proceeds, since a part of the hydrogen ions are converted by this reaction into water. In this way the acidity is diminished to the point where the reaction between the bromate and iodide is negligible during the time required for the titration.

The following procedure is used for the determination of iodates in the presence of bromates:

Procedure. Add 2 g. of potassium acid phthalate to 25 to 50 ml. of solution containing 2-3 milliequivalents of iodate, and swirl the mixture until all of the solid has dissolved. Add 3 g. of potassium iodide to the mixture and allow to stand for 3 minutes. Then titrate the liberated iodide with 0.1 N sodium thiosulfate solution to an end-point with starch indicator.

The pH of the pure phthalate solution is approximately 4, but this is increased to about 5 if 2.5 milliequivalents of iodate are present. An approximate ratio of 2 g. of potassium acid phthalate to 2.5 milliequivalents of iodate is necessary to give accurate results. A three-fold excess of hydrogen ion for the iodide-iodate reaction is essential, but a large excess of the phthalate must be avoided. If the approximate quantity of iodate in the sample is not known, a preliminary titration should be carried out to determine how much phthalate is to be added in the final determination.

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SOAP

Use: Detection of copper.

Detection of copper. Stea has stated that a green precipitate or coloration is formed when a solution of soap and formaldehyde is added to copper salts. Stea has made the claim that this reaction is characteristic for copper. According to Giorgio,[1,2] however, all metals except the alkalies give similar precipitates, and consequently the reaction is of little or no interest for the detection of copper.

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p-TOLUIC ACID

Synonym: 4-methylbenzoic acid

$C_8H_8O_2$ Mol. Wt. 136.14 Beil. Ref. IX, 483.

$$CH_3—C_6H_4—CO_2H$$

Use: Separation of calcium and strontium.

Determination of thorium.

p-Toluic acid is a white crystalline solid. It melts at 179-81° C. and boils at 274-275° C. It is only slightly soluble in hot water, but is very soluble in alcohol, ether and methyl alcohol.

Preparation. *p-Tolylcyanide:* Dissolve 50 g. of copper sulfate in 200 ml. of water in a 2-liter flask by heating on a water-bath, and add gradually 55 g. of potassium cyanide dissolved in 100 ml. of water.

Allow the above mixture to stand and dissolve 20 g. of *p*-toluidine in dilute hydrochloric acid. Cool in ice and stir well. Keep cool while gradually adding a solution of 16 g. of sodium nitrite in 40 ml. of water until the resulting mixture gives an immediate coloration with starch-potassium iodide paper. Add the resulting diazo solution in 10-ml. portions to the warm cuprous cyanide solution with frequent shaking. The addition of the diazo solution should take about 15 minutes. Then allow the mixture to stand on a water-bath until all effervescence ceases. Distill the mixture with steam (hood) and continue the distillation until a yellow oil no longer passes over. The tolylcyanide solidifies in the receiver as a yellow crystalline solid. Filter and dry on a porous plate.[1]

p-Toluic acid. Boil 10 g. of tolylcyanide with a mixture of 30 ml. of concentrated sulfuric acid and 20 ml. of water in a flask equipped with an upright condenser until colorless crystals of *p*-toluic acid appear in the condenser tube. The acid crystallizes from the mixture on cooling and is separated by filtration. Wash with water and recrystallize from hot water.[2]

Separation of calcium and strontium. Calcium and strontium may be separated in a 94 per cent acetone solution as the *p*-toluates. After the addition of 1 drop of 6 N ammonium hydroxide, a saturated solution of *p*-toluic acid gives a precipitate with strontium, while calcium yields no similar precipitate.[3]

Determination of thorium. Neish[4] reports that *p*-toluic acid gives a precipitate with thorium, but does not precipitate cerium, lanthanum, praseodymium or neodymium.

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RICINOLEIC ACID

$C_{18}H_{34}O_3$ Mol. Wt. 298.45 Beil. Ref. III, 385.

$$CH_3—(CH_2)_5—CH(OH)—CH_2—CH{=}CH—(CH_2)_7—CO_2H$$

Use: Determination of calcium.

This acid is present in castor oil, chiefly as an ester. It is a hard crystalline substance, which melts at 4-5° C. It is insoluble in water, but is soluble in alcohol, chloroform and ether. The commercial product is a yellowish, viscid mass.

Determination of calcium. Calcium may be determined nephelometrically as insoluble calcium ricinoleate.[1] Calcium is first separated from interfering substances, particularly magnesium, by precipitating as calcium oxalate. This is redissolved in acid and then determined with potassium ricinoleate.

Reagent. Dissolve 15 g. of potassium hydroxide in 125 ml. of 80 per cent alcohol and warm. Add 100 ml. of castor oil and reflux on a boiling water-bath until a sample dissolves completely in water without the separation of free oil. About 7 hours refluxing is required. Transfer 35 ml. of the castor oil soap solution to a 1-liter flask and add 9 g. of sodium hydroxide dissolved in 500 ml. of water. Dilute to 1 liter and mix well. This reagent should be perfectly clear and almost colorless. It is stable for about one week.

Procedure. Precipitate calcium oxalate in the usual manner, wash and dissolve in 5 ml. of 1:5 hydrochloric acid. Warm on a water-bath if necessary to dissolve the oxalate. Transfer to the flask in which the precipitation was originally carried out, rinsing with 5 ml. of distilled water. Shake the flask to dissolve any precipitate which adheres to the walls. In a second flask, place 10 ml. of standard calcium oxalate solution containing 0.15 mg. of calcium per ml., and then to both sample and standard add 20 ml. of the potassium ricinoleate reagent and mix well. Allow to stand for 2 minutes and compare nephelometrically. The cloud increases for 15-20 minutes, but as standard and sample are similar in composition this causes no error. This method is useful for quantities of calcium ranging from 0.75 to 2.5 mg.

The standard solution of calcium oxalate is prepared by dissolving 0.5475 g. of calcium oxalate monohydrate in about 500 ml. of 1:10 hydrochloric acid and diluting to 1 liter with 1:10 hydrochloric acid.

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SEBACIC ACID

$C_{10}H_{18}O_4$ Mol. Wt. 202.24 Beil. Ref. II, 718.

$$HO_2C—(CH_2)_8—CO_2H$$

Use: Determination of thorium.

Sebacic acid consists of white leaflets which melt at 132-133° C. The compound dissolves in 700 parts of water, but is freely soluble in alcohol and ether.

Preparation: Mix 100 g. of castor oil with 200 ml. of 40 per cent sodium hydroxide and allow to stand for several hours at 40° C. Press out and heat in an iron vessel for 3 hours with 1 molecular weight of solid sodium hydroxide until the mixture smells of capyrl alcohol. Then shake the mass with 3 liters of hot water and finally precipitate sebacic acid with hydrochloric acid.[1]

Determination of thorium. Thorium is quantitatively precipitated when a neutral aqueous solution of a thorium salt is boiled with sebacic acid. Thorium sebacate settles rapidly and is easily filtered. Cerium, lanthanum and yttrium give no precipitate under these conditions. The following method for determining thorium with sebacic acid has been proposed by Smith and James:[2,3]

Procedure. Heat 50 ml. of the thorium solution containing about 0.005-0.006 g. of ThO_2 per ml. to boiling and add a slight excess of a boiling, saturated solution of sebacic acid. The reagent solution should be added slowly and with constant stirring. Filter immediately, wash with boiling water, dry, ignite and weigh as ThO_2.

Kaufmann[4,5] has studied this method and states that while it gives good results, a preliminary isolation of thorium and the rare earths is necessary. When large quantities of cerium are present the method appears to be inaccurate. Kaufmann[5] recommends adding a solution of 3 g. of sebacic acid per 100 ml. of ethyl alcohol to the thorium solution. He also recommends evaporating the precipitate with fuming nitric acid, dissolving in water and precipitating again with sebacic acid. This operation is repeated until the precipitate is white, and then it is ignited and weighed.

Wenger and Duckert[6] do not recommend sebacic acid as a precipitant for thorium since it gives similar reactions with other metals.

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6. P. Wenger and R. Duckert, *Helv. Chim. Acta.* 25, 1110-14 (1942); *C.A.* 37, 575 (1943).

STEARIC ACID

$C_{18}H_{36}O_2$ Mol. Wt. 284.47 Beil. Ref. II, 377.

$$CH_3—(CH_2)_{16}—CO_2H$$

Use: Detection of lithium.
Determination of calcium, lithium, magnesium, nickel and sulfate.

Pure stearic acid consists of white leaflets which melt at 69-70° C. It is only very slightly soluble in water but is somewhat more soluble in benzene, chloroform, carbon tetrachloride, alcohol and acetone. It is also soluble in amyl acetate and toluene. U.S.P. stearic acid consists of a mixture of stearic and palmitic acids, and contains small quantities of unsaturated acids. It is obtained as a white or slightly yellow crystalline mass. It has a slight tallow-like odor and melts at about 55° C.

Detection and determination of lithium. Lithium stearate, unlike other alkali stearates, is relatively insoluble in organic solvents. This property has been used[1,2] for the detection and determination of small quantities of lithium.

Reagent. Dissolve 20 g. of stearic acid in 1 liter of ether and pass ammonia gas through the solution until ammonium stearate is no longer precipitated. Add a little ether from time to time to replace that lost by evaporation. Pour the suspension into a large dish and allow to stand until the ether has evaporated. Dissolve 2 g. of the ammonium stearate in 100 ml. of warm amyl alcohol. Do not heat above 50° C., since above that temperature ammonium stearate may be partially decomposed. This reagent must be prepared the day it is used.[3]

Procedure. Make the solution to be analyzed acid with hydrochloric acid and evaporate to a small volume and transfer to an Erlenmeyer flask. Add 10 ml. of amyl alcohol and heat on a sand-bath until all the water has been expelled, adding more amyl alcohol if necessary. Decant the solution of lithium chloride through a dry filter and wash the residue and filter with 3-ml. portions of hot amyl alcohol. Moisten the residue with 2 ml. of 1:1 hydrochloric acid and dissolve in 3 ml. of water. Evaporate to a small volume and repeat the extraction with amyl alcohol. Repeat 4 or 5 times if much lithium is present, although 2 times is usually sufficient when the quantity of lithium is small enough to necessitate a colorimetric method of estimation. Combine the amyl alcohol extracts and dilute to a suitable volume for use as the sample.

Place 2 ml. of the amyl alcohol solution in a test tube and prepare a series of standards with 0.05, 0.075, 0.1, 0.15, 0.25 and 0.4 mg. of lithium in 2 ml. of amyl alcohol. Now to sample and standards, add 5 ml. of ammonium stearate reagent in amyl alcohol. Stopper and shake standards and sample simultaneously. Allow to stand for 30 minutes, again shake and compare.

Determination of calcium. Calcium is estimated nephelometrically by precipitating as insoluble calcium stearate. This method has been used by various investigators for the determination of calcium in milk,[4-6] urine or blood:[7]

Ammonium stearate solution. Dissolve 4 g. of stearic acid and 0.5 ml. of oleic acid in 400 ml. of hot 95 per cent alcohol. Add 20 g. of ammonium carbonate dissolved in 100 ml. of water and boil for a few minutes. Allow to cool and add 400 ml. of 95 per cent alcohol, 100 ml. of water and 2 ml. of concentrated ammonium hydroxide. Upon filtering, the solution should be water-clear and colorless. Test the reagent as follows: Place 10 ml. of the standard calcium oxalate solution in one flask and 5 ml. in a second flask and to the 5 ml. portion add 5 ml. of 0.05 *N* nitric acid. Treat each with 25 ml. of the ammonium stearate reagent and determine whether one gives twice the reading of the other.

Standard calcium oxalate solution. Dissolve 0.0729 g. of pure calcium oxalate monohydrate in 25 ml. of 2 N nitric acid and dilute to 1 liter. Each ml. corresponds to 0.02 mg. of calcium in 0.05 N nitric acid.

Procedure. To determine calcium in blood or milk, precipitate as calcium oxalate in the usual manner, and dissolve the precipitate in 5 ml. of 0.1 N nitric acid. Transfer this solution to the flask in which the precipitation was originally carried out and shake to dissolve any precipitate which adheres to the walls of the vessel. Also rinse with 5 ml. of water the centrifuge tube and stirring rod which were used for the preparation and separation of the calcium precipitate. Place 10 ml. of the standard calcium oxalate solution in a second flask. Pipet 25 ml. of ammonium stearate reagent into each of two dry beakers and pour the standard solution into one of these and then pour the mixture back into the flask repeating the operation two times. Treat the sample solution in exactly the same way, and stopper both sample and standard. Shake well and allow to stand for 10 minutes. Compare nephelometrically.

Miloslavskii and Vavilova[9] report that in determining calcium nephelometrically as calcium stearate, a greater dispersion uniformity and stability of the turbidity are obtained by using a modified Lyman reagent. This is prepared as follows:

Reagent. Dissolve 4 g. of stearic acid and 0.5 g. of oleic acid in 425 ml. of 95 per cent alcohol by heating on a water-bath at moderate temperature. Dissolve 20 g. of ammonium carbonate in 100 ml. of water and add to the acid solution. Cool, add 425 ml. of alcohol, 50 ml. of water and 20 ml. of ammonium hydroxide. Filter and use the clear filtrate. For details of the determination, see section on oleic acid (page 48).

Stearic acid may be used for the determination of the hardness of water. The procedure is similar to that used with palmitic acid (page 73). Blacher and Jacoby[10] have used the following method:

Procedure. Determine bicarbonate hardness by titration with 0.1 N hydrochloric acid to an end-point with methyl orange in the usual manner. Expel the carbon dioxide with a current of air, neutralize to phenolphthalein with a few drops of N alcoholic potassium hydroxide and just decolorize with 0.1 N hydrochloric acid. Add an additional 1-2 drops of 0.1 N hydrochloric acid and determine the total hardness by titrating with 0.1 N potassium stearate.

The potassium stearate reagent is prepared by dissolving 28.4 g. of stearic acid in about 400 ml. of alcohol and 250 ml. of glycerol. Warm to aid solution. Neutralize the mixture with alcoholic potassium hydroxide, cool, and dilute with alcohol to 1 liter. Standardize the reagent against 10 ml. of calcium hydroxide solution that has been neutralized with 0.1 N hydrochloric acid.

Determination of sulfate. Sulfate is determined by a procedure based upon the fact that a neutral solution of potassium stearate is hydrolyzed in the presence of water to give an alkaline reaction to bromthymol blue, but upon the addition of barium chloride solution insoluble barium stearate is precipitated and the solution loses its alkalinity. Thus, when a solution containing a sulfate is titrated with barium chloride in the presence of potassium stearate the end-point may be detected by the disappearance of alkalinity in the presence of an excess of barium chloride.[11,12]

Reagent. Dissolve 3 g. of stearic acid in 22-23 ml. of 0.5 N alcoholic potassium hydroxide solution. Add 100 ml. of neutral 95 per cent alcohol and neutralize to phenolphthalein. Finally add alcohol to make the total volume 450 ml. and add 50 ml. of water.

Procedure. To 50-60 ml. of the sulfate solution, and 5.5 ml. of standardized barium chloride solution and 15 drops of bromthymol blue. Add 25 ml. of the potassium stearate reagent. Shake well and allow to stand for 30 seconds. If the solution is not distinctly bluish-green in color, add the potassium stearate reagent in 0.25-ml. portions and finally back titrate with barium chloride solution. The end-point does not occur when the theoretical amount of the reagent is added, and so it is necessary to standardize against known quantities of sulfate.

Cations such as aluminum, zinc, calcium and magnesium which form insoluble stearates must be absent. High concentrations of neutral salts such as sodium chloride and potassium chloride also interfere with the accuracy of the determination.

Determination of nickel. Quesada[13,14] recommends the use of stearic acid to retain colloidal nickel sulfide and colloidal sulfur.

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SUCCINIC ACID

$C_4H_6O_4$ Mol. Wt. 118.09 Beil. Ref. II, 601.

$$HO_2C—CH_2—CH_2—CO_2H$$

Use: Alkalimetric standard.

Detection of cerium, copper, lanthanum, nitrite, scandium, ytterbium and yttrium.

Separation and determination of iron and aluminum.

Succinic acid is a colorless to white crystalline compound, which possesses a very acid taste. It melts at 189-190° C., and boils at 235° C. with partial conversion to the anhydride. One g. of the solid dissolves in 13 ml. of cold water, 1 ml. of boiling water, 18.5 ml. of alcohol, 6.3 ml. of methyl alcohol, 36 ml. of acetone and 113 ml. of ether. It is insoluble in benzene, carbon disulfide and carbon tetrachloride. Its first dissociation constant is 6.6×10^{-5} and its second is 2.8×10^{-6}, both measured at 25° C.

Use as alkalimetric standard. Succinic acid has been used for the standardization of solutions of bases,[1-3,5-10] but is not recommended by Kolthoff[12] due to the ease with which it is converted into the anhydride on drying, and to the difficulty in obtaining it in a pure state. Phelps and Weed[7,8] recommend preparing the reagent by hydrolyzing succinic ester. The purity of the ester is determined by the fact that it distills within a temperature range of 0.2° C. Hydrolysis is carried out by boiling the ester for 4 hours with water containing a few drops of nitric acid in a flask equipped with a reflux condenser. The resulting solution is evaporated until crystals appear and the product is recrystallized from distilled water and dried in air to constant weight.

Peters and Sanchelli[10] report that they were unable to duplicate the results of Phelps and Hubbard[4,5] using ammonium hydroxide and cochineal. Ljungren[9] states that 0.1 N solutions of alkalies may be standardized correctly, provided the acid is dissolved in very little carbon dioxide-free water and not more than 10 ml. of solution is used. Only 3-4 drops of 1:1,000 phenolphthalein is used as the indicator and the titration is carried out to a faint pink color.

Separation and determination of iron. Ferric iron is precipitated quantitatively from neutral solutions as light brown ferric succinate by the addition of a neutral alkali succinate solution. Manganese, nickel, cobalt and zinc, however, are not precipitated by this treatment, which provides a method for the separation of iron from the divalent metals. The following procedure is used for this separation:[13]

Procedure. If the solution to be analyzed contains free acid, and all iron present is in the form of ferric salts, neutralize with ammonium hydroxide until a reddish-brown coloration appears, and then add sodium acetate until the solution is colored a deep brown. Dilute the mixture to 200 ml. for each 0.1 g. of iron present, and add 3 g. of sodium succinate dissolved in a little water. Heat nearly to boiling, filter, and wash with a little cold water. Finally wash with warm N ammonium hydroxide solution until 20 drops of the filtrate leaves no residue when evaporated to dryness on a platinum strip. During the washing with ammonium hydroxide, ferric succinate is converted into ferric hydroxide, which in turn is converted to ferric oxide by ignition in a porcelain crucible.

Aluminum is precipitated with iron and must either be absent in determining iron by this procedure, or must be separated from iron in the residue and the quantity of iron present determined by difference.

Hanus and Vorisek[14] have compared the acetate, succinate and hexamethylenetetramine methods for separating iron from nickel and report that for solutions having a Fe:Ni ratio greater than 40, iron may be separated by a double precipitation using the acetate or succinate methods.

Separation and determination of aluminum. Aluminum is separated from large quantities of manganese, cobalt, nickel, zinc, iron, cadmium, copper, calcium, barium, and magnesium by precipitating as the basic succinate. This is formed by boiling the acid aluminum solution which contains urea and succinic acid. Hydrolysis of urea gradually brings about the formation of ammonia in a homogeneous solution and gives a pH of 4.2-4.6. The precipitate formed in this way is dense and is much more easily filtered and washed, and shows less adsorption of other salts than does the aluminum precipitate obtained by the usual methods.

Willard and Tang[15] recommend the following procedure for the precipitation and determination of aluminum:

Procedure. To an acid solution containing about 0.1 g. of aluminum, add ammonium hydroxide until a slight turbidity appears, and carefully add dilute hydrochloric acid until the solution is clear, and then add 1-2 drops in excess. Dilute with a little water, and add 5 g. of succinic acid dissolved in 100 ml. of water. Add 10 g. of ammonium chloride and 4 g. of urea. Dilute to about 250 ml., heat to boiling and boil gently for two hours after the solution has become turbid. Allow the mixture to stand for a few minutes, and add a little paper pulp. Filter, and wash 10 times with a 1 per cent succinic acid solution that has been neutralized to methyl red with ammonium hydroxide. Ignite in a platinum crucible at 1200° C. to constant weight.

By the above procedure, 0.1 g. of aluminum may be separated from 1 g. of calcium, barium, magnesium, manganese or cadmium in a single precipitation from a total volume of 250 ml. of solution. The method is effective for separating 0.1 g. of aluminum from an equal weight of nickel or cobalt, or a few mg. of aluminum from as much as 1 g. of nickel or cobalt. A double precipitation is recommended, however, to separate 0.1 g. of aluminum from 1 g. of nickel or cobalt.

The separation of aluminum and copper is incomplete due to the low solubility of copper succinate. If, however, copper is kept in the cuprous state with ammonium bisulfite during the precipitation, the separation is satisfactory. Aluminum and iron may be separated by this method, but iron must be reduced to the ferrous state, preferably with phenylhydrazine. Aluminum and zinc may also be separated, but two precipitations are recommended.

Boyle and Musser[16] recommend a modification of Willard and Tang's[15] basic succinate method for the determination of aluminum in magnesium alloys. The following method is taken directly from the published work of Boyle and Musser: *

Reagent. Dissolve 10 g. of urea, 5 g. of ammonium chloride and 5 g. of succinic acid in water and dilute to 300 ml.

Procedure. Weight a 1 g. sample of the alloy into a 600 ml. beaker. Treat with 50 ml. of distilled water and 10 ml. of concentrated hydrochloric acid. After the alloy is dissolved, filter to remove metallic copper. Interference due to appreciable amounts of iron is prevented by adding to the heated filtrate a few drops of a 10 per cent solution of ammonium bisulfite and 2 ml. of phenylhydrazine. This treatment serves to reduce the iron and to maintain it in a ferrous state during the precipitation of aluminum as basic succinate. Dilute with 300 ml. of succinate reagent and boil gently. Make the solution just alkaline to methyl orange with freshly filtered 1:1 ammonium hydroxide or a solution of ammonium carbonate. Continue boiling gently for 90 minutes, precipitating the aluminum as the basic succinate. Gentle boiling is very effective and does not reduce the total volume quickly. No special care need be given the solution during this period.

Filter through a paper of loose texture. Dissolve the small amount of precipitate which adheres to the beaker in 20 ml. of 1:4 hydrochloric acid and reprecipitate by adding 1:1 ammonium hydroxide until just alkaline to methyl red. Boil the solution for one minute and filter through the paper containing the major portion of the precipitate. Wash the precipitate six times with hot one per cent ammonium chloride made alkaline to methyl red with ammonium hydroxide. Ignite the precipitate at 1300° C. for one hour to form nonhygroscopic corundum, cool, and weigh as the oxide. Unglazed porcelain crucibles appear to be best for this purpose since they show no change in weight. For long life of the crucible it is advisable to dry the crucible and precipitate in a standard oven before ignition. For rapid rountine analysis, it is preferable to brush the precipitate out of the crucible and weigh directly as oxide.

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If silicon is present in quantities greater than 0.2 per cent, dissolve the alloy in 30 ml. of 1:2 perchloric acid. Evaporate the solution on a hot plate to copious fumes of perchloric acid. Cool, dilute to 50 ml. with distilled water, and filter through a fast paper. Wash the precipitate six times with hot distilled water and discard. Copper is dissolved by this procedure. In order to eliminate the error due to this element, add 20 ml. of the ammonium bisulfite reagent to the solution, or (if iron is absent) 1 g. of hydroxylamine. Add 300 ml. of the succinate reagent and continue as described previously.

Detection of copper. Martini[17] has used succinic acid for the microchemical detection of copper. This consists in mixing one drop of the solution containing copper as the chloride with a small drop of a saturated solution of succinic acid and a little ammonium hydroxide. Copper is indicated by green crystals which form. These are probably copper ammonia succinate. Various amines can be used to replace the ammonium hydroxide.

Detection of the rare earths. As little as 1γ each of yttrium, lanthanum, ytterbium and scandium can be detected with the use of ammonium succinate. Martini[11,18] regards this reaction as more sensitive than those with sodium sulfate, potassium sulfate, rubidium chloride, cesium chloride and potassium ferrocyanide.

Behrens and Kley[19] have suggested succinic acid as a reagent for cerium, but this test is not recommended by Wenger and Duckert[21] since it is too general.

Detection of nitrite. Salei[4] has recommended the use of succinic acid in a modified Griess reagent for nitrites.

Reagent. Grind in a mortar to a fine powder a mixture of 0.1 g. of α-naphthylamine, 1 g. of sulfanilic acid and 5 g. of succinic acid. This dry reagent is stored in a dark glass bottle which is fitted with a ground glass stopper.

If necessary the solid may be dissolved in 300 ml. of water. This reagent compares favorably with that containing acetic acid in the time of appearance of the color.

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CHAPTER II

HALOGEN SUBSTITUTED ACIDS

p-BROMOBENZOIC ACID

$C_7H_5O_2Br$ Mol. Wt. 201.03 Beil. Ref. IX, 351.

$Br—C_6H_4—CO_2H$

Use: Detection of strontium.

Determination of calcium and strontium.

p-Bromobenzoic acid is a crystalline solid melting at 251-252° C. It is soluble in alcohol and ether but is almost insoluble in cold water.

Preparation: *Bromotoluene:* Mix toluene with 10 per cent its weight of iodine and the calculated quantity of bromine and allow the mixture to stand at ordinary temperature for 12 hours. Wash with sodium hydroxide and water and fractionally distill. Collect the fraction boiling at 180-190° C.

p-Bromobenzoic acid: Mix 150 g. of *p*-bromotoluene with 400 g. of potassium dichromate and 500 g. of sulfuric acid and boil for 12 hours under reflux. Dilute the mixture with twice its volume of water and remove any unoxidized oil by distillation with steam. Purify the product by washing with water and converting to the sodium salt.[1]

Separation of calcium and strontium. Bailar[2] has studied the reactions of *p*-bromobenzoic acid with the alkali and the alkaline earth metals. The alkali and ammonium *p*-bromobenzoates are soluble to the extent of about 1 per cent in acetone containing 6 per cent water. When 15 ml. of a saturated solution of ammonium *p*-bromobenzoate in 94 per cent acetone is added to 1 ml. of an aqueous solution of strontium nitrate containing as little as 1 mg. of the salt per ml., a distinct precipitate is formed. A solution of calcium nitrate which is 50 times as concentrated as the strontium solution remains perfectly clear when similarly treated. The solubility of the strontium salt, however, is increased remarkably by the presence of other metallic salts including calcium. If the concentration of calcium nitrate is only 3-4 times that of strontium nitrate, and both salts are present in the same solution, no precipitate is formed. It appears, therefore, that the reagent is not satisfactory for the separation of calcium and strontium, although it may offer some advantages as a reagent for strontium alone.

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CHLOROACETIC ACID

Synonym: Monochloroacetic acid

$C_2H_3O_2Cl$ Mol. Wt. 94.50 Beil. Ref. II, 194.

$CH_2Cl—CO_2H$

Use: Determination of zinc.

Chloroacetic acid consists of white or colorless deliquescent crystals. The compound exists in three physical modifications which have different melting points. The commercial product melts at 62-64° C. The compound is very soluble in water, alcohol, chloroform and ether. It should be stored in a tightly stoppered bottle and in a cool place.

Preparation: Place 100 g. of glacial acetic acid and 10 g. of sulfur in a small flask and weigh. Fit the flask with a 2-hole rubber stopper holding a reflux condenser and a delivery tube, which extends down into the acid. Heat the flask on a boiling water bath, and pass a steady stream of chlorine into the acid until the weight of the flask and contents has increased 50 g. This requires about 6 hours. The chlorination should be carried out in direct sunlight. When chlorination is complete, decant the liquid from the sulfur into a distilling flask, and distill through an air condenser. Collect the fraction boiling at 150-190° C. Crystals of chloroacetic acid separate on cooling. Drain off the liquid from the crystals, and redistill the latter. Collect the fraction boiling at 180-190° C.

Determination of zinc. Chloroacetic acid has been used to adjust the pH of a solution for the precipitation of zinc as zinc sulfide.[1,2] In this way zinc may be separated from iron, cobalt and nickel. The separation is carried out by heating the solution having a total volume of 450 ml. to 50-60° C., adding 4 ml. of 2 N ammonium hydroxide and 7 ml. of 4 N chloroacetic acid solution, and treating with hydrogen sulfide. In this way a good separation of 0.3-0.5 g. of zinc oxide may be effected.

1. P. v. Berg, *Z. anal. Chem.* **25**, 512-19 (1886).
2. E. Azzarello, A. Accardo and F. Abramo, *Atti V congr. naz. chim. pura applicata, Rome,* 1935. **II**, 658 (1936).

o-CHLOROBENZOIC ACID

$C_7H_5O_2Cl$ Mol. Wt. 156.57 Beil. Ref. IX, 334(138).

$Cl—C_6H_4—CO_2H$

Use: Standard in alkalimetry and iodometry.

o-Chlorobenzoic acid is obtained as colorless crystalline needles which melt at 139-140° C. It is easily soluble in hot water, alcohol and ether.

Preparation: Dissolve 13.7 g. of anthranilic acid in a mixture of 30 ml. of concentrated hydrochloric acid and 75 ml. of water and cool to about 0° C. Diazotize by adding slowly 7 g. of sodium nitrite dissolved in 25 ml. of water. The resulting diazo solution is slowly added with shaking to an ice cold solution of cuprous chloride, prepared by boiling 7 g. of cupric chloride in a mixture of 50 ml. of concentrated hydrochloric acid and 50 ml. of water with 4-5 g. of copper. Allow the mixture to stand for 4-5 hours at ordinary temperature and filter. Wash the crystals of *o*-chlorobenzoic acid with a little water, and purify by dissolving in hot water containing a little alcohol and animal charcoal and boiling. Filter hot and collect the crystals which separate from the filtrate.[1]

o-Chlorobenzoic acid may also be prepared from *o*-chlorotoluene by the following method:

In a 12-liter flask, fitted with a stirrer and reflux condenser, place 600 g. of potassium permanganate, 7 liters of water and 200 g. of *o*-chlorotoluene. Slowly heat to boiling, and keep at this temperature until the color disappears. This requires about 3-4 hours. Distill the mixture until no oil passes over with the water. Filter hot, with suction, and wash the residue of hydrated manganese dioxide with two 500-ml. portions of hot water. Concentrate the combined filtrate and washings to 3.5 liters, and clarify with 1-2 g. of decolorizing charcoal. While still hot, acidify by the cautious addition of 250 ml. of concentrated hydrochloric acid with agitation. Cool, filter, and wash the residue with cold water. Purify by recrystallizing from 600 ml. of toluene.[4]

***o*-Chlorobenzoic acid as a standard in iodometry.** The reaction

$$IO_3^- + 6H^+ + 5I^- \rightarrow 3I_2 + 3H_2O$$

is used for the standardization of sodium thiosulfate solutions, and results obtained using this method are accurate to within 0.1 per cent of theoretical. The following procedure is suggested by Murgulescu and Latui [2] for the standardization of sodium thiosulfate:

Procedure. Dissolve 0.5 g. of *o*-chlorobenzoic acid in 8-10 ml. of ethyl alcohol and add 5-7 ml. of N potassium iodide and 5-7 ml. of 3 per cent potassium iodate solution. Titrate the resulting mixture with the thiosulfate solution to a starch end-point.

156.57 g. of *o*-chlorobenzoic acid is equivalent to 126.92 g. of iodine.

***o*-Chlorobenzoic acid as a standard in acidimetry.** An approximately 0.1 N solution of sodium hydroxide can be standardized by means of the following procedure: [3]

Procedure. Weigh out 0.3-0.6 g. of *o*-chlorobenzoic acid and dissolve in 7-15 ml. of ethyl alcohol, and dilute with 12-14 ml. of water. Add 2 drops of a 0.2 per cent solution of methyl red in 60 per cent ethyl alcohol for each 10 ml. of solution, and titrate the cold solution until the indicator begins to fade. Then boil for 2 minutes, cool, and complete the titration. The equivalent weight of *o*-chlorobenzoic acid is 156.57.

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1. C. Graebe, *Ann.* **276**, 54 (1893).
2. I. G. Murgulescu and E. Latui, *Z. anal. Chem.* **125**, 267-68 (1943); *C.A.* **37**, 4320 (1943).

3. I. G. Murgulescu and V. Alexa, *Z. anal. Chem.* **125**, 260-67 (1943); *C.A.* **37**, 4320 (1943).
4. H. T. Clarke and E. R. Taylor, *Organic Synthesis,* **10**, p. 20.

TRICHLOROACETIC ACID

$C_2HO_2Cl_3$ Mol. Wt. 163.40 Beil. Ref. II, 206.

CCl_3CO_2H

Use: Determination of fluoride.

Trichloroacetic acid consists of colorless, very deliquescent crystals, having a slight characteristic odor. It melts at 54-57° C. and boils at 196-197° C. It is soluble in water, alcohol and ether. The acid is very corrosive.

Preparation: Melt 25 g. of chloral hydrate in a distilling flask and add 20 g. of fuming nitric acid ($d = 1.5$). Heat the mixture cautiously over a free flame until the reaction begins. When red fumes are evolved, the reaction proceeds without the application of heat. When fumes are no longer given off on heating the mixture, the reaction is complete. Collect the fraction boiling between 123-194° C., which consists of nitric acid and trichloroacetic acid. The pure acid distills at 194-196° C. Distill the last fraction, using only a condenser tube. Treat the fraction boiling at 123-194° C. with an additional 10 ml. of fuming nitric acid, and purify the product as before.[1,2]

Determination of fluoride. Trichloroacetic acid which has been one-half neutralized with sodium hydroxide is used as a buffer for the determination of fluoride with thorium nitrate and alizarin S.[3] See section on alizarin S.

1. Dumas, *Compt. rend.* 8, 609 (1838).
2. Clermont, *Ann. Chim. Phys.* [6] **6**, 135 (1871).
3. R. J. Rowley and H. V. Churchill, *Ind. Eng. Chem., Anal. Ed.* **9**, 551 (1937); *C.A.* **32**, 880 (1938).

CHAPTER III

HYDROXY ACIDS

AURIN TRICARBOXYLIC ACID (AMMONIUM SALT)

Synonym: Aluminon

$C_{22}H_{14}O_9$ Mol. Wt. 422.33 Beil. Ref. X, 1050.

$$O{=}C_6H_3(CO_2H){=}C{=}(C_6H_3(OH)CO_2H)_2$$

Use: Detection of aluminum, gallium, scandium and thorium.

Determination of aluminum and fluoride.

The sodium salt of aurin tricarboxylic acid is marketed under the names "chrome rubine" or "chrome violet." The ammonium salt is known as "aluminon." The crude dye may be extracted with hot water, converted to the ammonium salt with ammonium hydroxide, and recovered by evaporation to dryness.

The compound occurs as a red powder which possesses a metallic luster (from dilute alcohol).

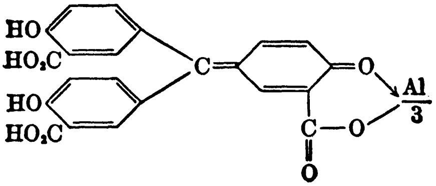
Preparation: Place 44 ml. of sulfuric acid (d = 1.84) in a 250-ml. beaker, and add in small portions and with vigorous stirring 4 g. of sodium nitrite. Add the nitrite slowly so that there will not be excessive evolution of the oxides of nitrogen. When all the nitrite is dissolved, cool to 10° C. During a period of 5-10 minutes, add 12 g. of salicylic acid with vigorous stirring. Cool the mixture to 3° C. by immersing in crushed ice, and add dropwise 3.5 ml. of approximately 37 per cent formaldehyde. Stir vigorously during the addition of the aldehyde. It is convenient to stir with a small thermometer, since during this operation the temperature must not exceed 5° C. Allow the beaker to remain in the ice bath one hour after all the formaldehyde has been added, and stir the contents every 5 minutes. Allow the reaction to proceed at reduced temperature for 20 hours. A cooling bath 12 inches square and 3.5 inches deep containing 20 pounds of ice and filled with ice water serves to keep the temperature sufficiently low for the 20 hour period. The beaker containing the reaction mixture is placed in a corner of the ice bath and weighted to prevent tipping.

After 20 hours, slowly pour the contents of the beaker into 2 liters of cold distilled water with constant stirring and allow the mixture to stand for one hour. Filter, using a Büchner funnel and 15-cm. paper of close texture. Wash the precipitate 3 times with distilled water, and return to the beaker in which the precipitation was originally carried out. Add one liter of water and 50 ml. of hydrochloric acid ($d = 1.18$) and boil for 2-3 minutes. Let the precipitate settle for 10 minutes and wash 3 times by decantation with distilled water. Break up the black mass thoroughly with a stirring rod, and repeat the boiling treatment with one liter of water and 50 ml. of hydrochloric acid, followed by washing with water two more times.

Finally, dissolve the residual mass in an excess of ammonium hydroxide and evaporate to dryness on a steam bath. Grind the residue to a fine powder and transfer to a bottle.[2,33]

Analytical reactions. In 1925 Hammett and Sottery[1] proposed the use of the ammonium salt of aurin tricarboxylic acid as a sensitive reagent for aluminum, with which it reacts to form a red lake. Many ions interfere by forming similar lakes, but the interference by many of these ions may be eliminated by use of the unusual property of the aluminum lake that, although it does not form in an alkaline solution, once formed in an acetic acid-acetate buffer solution it is not decomposed immediately when the solution is made alkaline with ammonium hydroxide. The chromium lake, for example, which resembles that of aluminum in appearance, forms in an acetic acid-acetate buffer, but it is decolorized upon the addition of ammonium hydroxide.

Many metallic ions react with aluminon to form chelate compounds of the type indicated by that of the aluminum complex.



The exact composition of the lakes which aluminon forms with aluminum and other metals is, however, unknown. Thrun[2] has studied the metallic lakes of the reagent and concludes that these are of two types: the first occurs when the acid form of aluminon (red) is adsorbed by a hydrous oxide which is insoluble in a slightly acid solution; and the second is formed when the anhydride is adsorbed by an insoluble base such as ferric hydroxide in the absence of ammonium salts, or by a negative hydroxide like titanic oxide in the presence of ammonium salts. Since chelate salts do form with aluminon, however, it is likely that the formation of these compounds plays some part in lake formation.

Other ions which react with aluminon to yield red colors or precipitates in an alkaline medium are actinium, barium, beryllium, calcium, cerium, chromium, erbium, gallium, hafnium, indium, iron, lanthanum, magnesium, neodymium, radium, scandium, strontium, thorium, yttrium, and zirconium. White precipitates also form with antimony, bismuth, lead, mercury, silicic acid, and titanium. Aluminon may be used for the detection and determination of many of these ions.

Detection of Aluminum. The red lake which forms when aluminon is added to solutions of aluminum salts has been used as a method of detecting aluminum. The test may be applied to precipitated aluminum hydroxide by using the following procedure:[1]

Reagent. Dissolve 0.25 g. of aurin tricarboxylic acid in a few drops of ammonium hydroxide and evaporate to dryness on a steam bath. Dissolve the residue in 250 ml. of distilled water. An equivalent amount of the ammonium salt of aurin tricarboxylic acid may be used.

Procedure: Dissolve the precipitate of aluminum hydroxide in 5 ml. of N hydrochloric acid and add 5 ml. of 3 N ammonium acetate and 5 ml. of the reagent. Mix well and allow to stand for a few minutes until the lake forms, and then make the solution alkaline with ammonium hydroxide containing ammonium carbonate. A bright red precipitate which persists in the alkaline solution indicates the presence of aluminum.

As little as 0.0005 g. of aluminum gives an immediate precipitation. Smaller quantities cause precipitation or a red solution, which is easily distinguished from the yellowish alkaline solution of the reagent. The sensitiveness of the test is approximately 2.5γ. Roller[4] reports that this reaction may be made more sensitive if carried out at a pH of 6.3 instead of in an alkaline solution as suggested by Yoe and Hill.[8]

Silicic acid and salts of bismuth, lead, antimony, stannic tin, mercuric mercury, and titanium yield white precipitates under the conditions of the test. Salts of cadmium, cobalt, manganese, nickel, and zinc, however, do not precipitate. Alkaline earths, if present in high concentration, give red preciptates, but these are decolorized by the ammonium carbonate. Ferric salts give a deep violet precipitate in an acetic acid solution, and this is converted to a reddish-brown by ammonium hydroxide. Iron may be separated from the aluminum by means of sodium hydroxide or peroxide. A large excess of phosphate prevents the formation of the aluminum lake. By adding ammonium hydroxide to a solution containing phosphate and aluminum, aluminum is precipitated as aluminum phosphate, and this is filtered off, dissolved in acid, and used for making the test. In this way excess phosphate is removed. Porcelain vessels should not be used with alkalies while making this test, since the amount of aluminum which dissolves by this treatment is usually sufficient to give the test with aluminon.

Korenman[5] has proposed a more sensitive flotation method based on the aluminon reaction.

Reagents: *Buffer solution:* Dissolve 78 g. of ammonium acetate, 54 g. of ammonium chloride, and 60 ml. of 1:1 hydrochloric acid in water and dilute to one liter.

Aluminon solution: This is a concentrated aqueous solution of ammonium aurin tricarboxylate.

Procedure: Make 5 ml. of the sample slightly alkaline with ammonium hydroxide, and make slightly acid with acetic acid. Add 2-3 ml. of the buffer solution and 3-4 drops of the aluminon reagent, and shake the mixture with 1 ml. of chloroform. The presence of aluminum is shown by a red film at the zone between the aqueous layer and chloroform.

In this procedure, ferric iron is reduced before making the test. Other cations of group III do not interfere. Yoe [6] suggests that the iron be completely removed before making test. Small quantities of iron are successfully removed by co-precipitation with relatively large amounts of copper. Precipitation with sodium hydroxide or sodium sulfide, followed by digestion for 30-60 minutes on a steam bath, is also satisfactory.

A spot reaction based on the aluminum-aluminon reaction has been proposed by Thrun.[7]

Reagent. Strips of ashless filter paper are immersed in a 0.1 per cent solution of aluminon and dried. Not all filter paper is satisfactory for this purpose. Those grades recommended are S and S No. 598, Delta No. 316, and Munktells No. 1 F.

Procedure. Acidify with dilute hydrochloric acid a portion of the filtrate obtained in the regular analytical procedure where aluminum, chromium, and zinc are separated as $NaAlO_2$, Na_2CrO_4, and Na_2ZnO_2. Place a drop of this acidified solution on a strip of test paper, and, after one minute, hold the moist spot above the open mouth of a bottle of ammonium hydroxide for 10 seconds and allow to dry. After one hour, the presence of aluminum is indicated by a deeper pink spot.

Interference with this test is essentially the same as indicated in the above tests.

Dobbins and Southern [32] and Davies [34] have used aluminon as a confirmatory test for aluminum in a systematic scheme of analysis. This reaction has also been used in a spot test for the detection of aluminum in steel.[36]

Determination of aluminum. The aluminon test of Hammett and Sottery [1] has been shown by Yoe and Hill [8] to be adaptable to the quantitative determination of aluminum. In fact, in the light of more recent studies it appears that aluminon is the most satisfactory reagent for the determination of small quantities of aluminum. Its most important advantage lies in the almost complete absence of color when added in excess to aluminum solutions under conditions of the test. A careful study of quantitative methods based on the use of aluminon, however, reveals that many factors may seriously affect the result, and that a given procedure must be very carefully followed in order to obtain satisfactory results. Yoe and Hill [8] report that factors of time, temperature, volume, concentration, and the presence of other ions may affect the result.

While most commercial samples of aluminon are suitable for the detection of aluminum, very few give satisfactory results when used for the colorimetric determination of this element. According to Scherrer and Smith,[3] a satisfactory grade of aluminon must show a definite pink color with 0.2 mg. of aluminum in a volume of 50 ml., and only a slight straw color if aluminum is absent. Most commercial grades yield solutions which are unstable; others produce "muddy" precipitates; and all are too deeply colored in the absence of aluminum. For these reasons, careful attention to the preparation of the reagent is essential for a satisfactory determination. The method of preparation described above yields a satisfactory quantitative reagent.

A dilute neutral or slightly acid solution of aluminon is yellowish-brown in color, but becomes pale yellow when made basic. Aurin tricarboxylic acid is precipitated on the addition of a mineral acid.

In acetate-buffered acetic acid solutions, or in neutral solutions, aluminon gives a deep red color with very small quantities of aluminum. In some procedures the color produced in acid solutions is measured or compared without further treatment. In some cases, however, the solution is made basic with ammonia before comparison. Advantages claimed in making the solution alkaline are the weaker color of the excess reagent in a basic medium, and the possibility of reducing interference with such metals as chromium. It is claimed, however, that the reaction is less sensitive in a basic medium, and the lake becomes less stable. Various metals may also be precipitated under these conditions. In the investigation of aluminum in plants, Winter, Thrun and Bird [13,20] conclude that the maximum color is obtained in the presence of 10 per cent ammonium acetate when the solution is maintained at 80° C. for 10 minutes and at approximately pH 4. Roller [4] claims that the color is much more sensitive if developed at pH 6.3 instead of in an alkaline solution as recommended by Yoe and Hill.[8] Roller [4] and others [10,13,14,39] recommend making the determination in an acid medium. The following method is recommended by Roller: [4]

Procedure. Adjust the pH of the sample solution to 6.3 and dilute with distilled water to 12 ml. Add 5 ml. of a buffer of pH 6.3 prepared from 4 M ammonium acetate and hydrochloric acid. Shake well, and for each 0.01 mg. of aluminum add 1 ml. of 0.1 per cent solution of aluminon. Shake, allow to stand 15 minutes for maximum color development, and compare with standards. With less than 0.002 mg. of aluminum, use Nessler tubes for the comparison.

As much as 10 mg. of barium, calcium, lead, magnesium and zinc; 0.1 mg. of cobalt and copper; and 5 mg. of phosphate ion, all in a volume of 18 ml. give no color. The color obtained with 0.1 mg. of chromium is equivalent to 0.0005 mg. of aluminum and 0.01 mg. of ferric iron gives the same color as 0.005 mg. of aluminum.

Sandell [39] recommends a similar method for determining 1-25γ of aluminum in which the pH of the solution is brought to about 5.5 with ammonium acetate.

Procedure: Place 5-10 ml. of solution containing 1-25γ of aluminum in a 25-ml. volumetric flask and add 1.0 ml. of 1:9 hydrochloric acid. The sample solution should contain no acetate or other buffer. Add 1.0 ml. of 0.2 per cent aqueous aluminon solution, dilute to about 15 ml. and add 5 ml. of 10 per cent ammonium acetate solution. Dilute to the mark with water, allow to stand 15 minutes and determine the transmittancy with a green filter (circa 520 mμ).

Recently Musakin [10] studied the effect of pH, concentration of aluminum ion, concentration and quality of the reagent, time, and presence of other ions upon the intensity of the color of the aluminum lake, and has suggested the following procedure for determining approximately 0.1 mg. of aluminum:

Reagents: *Buffer solution:* Dissolve 175 mg. equivalents of sodium acetate and 25 mg. equivalents of hydrochloric acid in water and dilute to one liter. This solution has a pH of 5.5.

Aluminon solution: Dissolve 0.1 g. of aluminon in 100 ml. of water and allow to stand for several days in the dark.

Procedure. To a neutral solution containing up to 0.1 mg. of aluminum ion (which has been freed from ferric ions by a double treatment with 1 ml. of 30 per cent potassium thiocyanate and 1 ml. of amyl alcohol) add 20 ml. of the buffer solution and 2 ml. of the aluminon reagent and dilute to 32 ml. Allow to stand for one hour, or preferably overnight, and compare with a standard prepared under identical conditions. The results are calculated from an experimentally determined curve showing the intensity of coloration as a function of concentration.

Typical of the methods which have been proposed for comparing the color of the aluminum lake with aluminon in an alkaline medium is that proposed by Scherrer and Mogerman. This method has been applied to the determination of aluminum in non-ferrous metals. Satisfactory results are obtained if directions are carefully followed. The range in which the method is applied is from 0.02-0.08 mg. of aluminum. According to their procedure most interfering metals are removed by electrolysis in a mercury cathode. A modified Melaven cell[12] is used with vigorous stirring. About 50 ml. of mercury and a current of 3-5 amperes is suitable. Practically all interfering metals are removed by using as an anode a platinum wire which projects into the solution about 12 cm.

Procedure. Dissolve a quantity of sample containing 0.02-0.08 mg. of aluminum in 5 ml. of sulfuric acid, dilute to 25 ml. and filter. Electrolyze the filtrate as described above, and after electrolysis is complete, remove the solution and filter. Separate from the mercury while at least a part of the current is on.

To the solution obtained by the above treatment (which should have a volume of 40-75 ml.) add 5 ml. of concentrated hydrochloric acid, 5 ml. of glacial acetic acid, and 5 ml. of a 0.2 per cent aqueous solution of aluminon. Mix well and add ammonium hydroxide dropwise until the cloudy appearance of the dye disappears and the solution becomes clear, although still acid to litmus and still deeply colored. Place a piece of litmus paper against the inner surface of the beaker, and with constant stirring add ammonium hydroxide at the rate of one drop every 2 seconds until 2 ml. have been added, and then one drop every 3-4 seconds until the litmus turns blue. Next add 5 ml. of glacial acetic acid and allow the mixture to stand 10 minutes. Neutralize as before and add a final 5 ml. of ammonium hydroxide. Allow the solution to cool to room temperature, and compare the color with that of standard solutions similarly prepared.

If the comparison is made in 150-ml. beakers against a white background, a difference of 0.01 mg. of aluminum can be distinguished. The rate of addition of ammonium hydroxide affects the results materially, and for this reason that part of the procedure describing this operation should be carefully followed.

A number of metals interfere, especially iron and beryllium which also yield red lakes with aluminon. This interference cannot be prevented, and the metals must be removed. The use of ammonium carbonate with, or in place of, ammonium hydroxide prevents interference by the alkaline earths, rare earths and zirconium in quantities not exceeding 10 mg. per 100 ml., and also by thorium and chromium. Magnesium at a concentration of 10 mg. per ml. gives a pink color which is not discharged by ammonium carbonate, but at concentrations lower than this value interference is prevented by ammonium carbonate. Gallium at a concentration of 0.1 mg. per 100 ml. does not interfere, but at higher concentrations yields a red color. Quantities of indium and thallium not exceeding 2 mg. are without effect. Tetravalent vanadium must be absent, but pentavalent vanadium does not interfere if the quantity does not exceed 1 mg. Small quantities of arsenic, cadmium, germanium, lead, molybdenum, titanium, tungsten and zinc do not interfere. Ruthenium yields a colored solution, and platinum gives a yellow chloroplatinate. Gold is reduced to the metal.

Fluoride, hydrogen sulfide, nitric acid and sulfur dioxide discharge the red color, but this interference may be eliminated by evaporating with sulfuric acid until fumes of sulfur trioxide appear. Phosphoric acid in quantities below 25 mg. per 100 ml. is without effect, but at higher concentrations causes a reduction of the color intensity.

Aluminon is more convenient as a reagent for aluminum than alizarin, since with the latter a highly colored anion of the dye appears with increase in the pH of the solution.[14] The use of aluminon permits a wider variation in pH, shows a greater stability toward the action of buffer solutions, and a greater molar absorption coefficient.

According to Peshkova[15] the color of the aluminum-aluminon lake varies somewhat if alkali or alkaline earths are present. Schwartze and Hann[16] report that better results are obtained in determining minute quantities of aluminum by using a spectrophotometer instead of a colorimeter. Prideaux and Henness[17] have used aluminon for the determination of aluminum in the study of the hydrous oxides of aluminum.

A number of special methods have been developed for the determination of aluminum in various materials:

Biological Materials.[43,44]
Non-ferrous Metals.[11,18]
Blood.[19]
Plants and Plant Materials.[20,21,23,85]
Steel.[22,37]
Foods.[24,41,42]
Leach Liquors.[88]

Reactions of aluminon. Middleton[25] has studied the lake formation of aluminon with various cations, and has found that the reagent forms lakes with the hydroxides or basic acetates of beryllium, yttrium, cerium, lanthanum, neodymium, erbium, zirconium, and thorium, and these are similar to the lakes formed with aluminum. All of the above are of a deeper red than that of aluminum, but are likely to be confused with the latter. In all cases the lakes of the above metals are less soluble than the corresponding hydroxides or basic acetates. Lakes of the above metals, excepting that of beryllium, are decolorized by ammonium carbonate. Aluminon does not distinguish aluminum from beryllium in mixtures of the two.

Corey and Rogers [26] report that indium reacts with aluminon to yield a red solution which is relatively stable in the presence of ammonium hydroxide, although no precipitate is formed. The color is discharged by ammonium carbonate. Germanium and thorium form no stable lakes with the reagent and in this respect resemble silicic acid, stannic tin and lead. A thallium lake forms only with difficulty and is unstable in ammonium hydroxide and ammonium carbonate.

Yoe [6] has made a rather complete study of the reactions of many ions with aluminon. The tests were carried out as follows:

The solution to be tested was of such concentration that the solution at final dilution contained 20 p.p.m. metallic ion.

The reagent used was a 0.1 per cent aqueous solution of aluminon.

Procedure. To a measured amount of solution to be tested, reagents were added in the following order: (1) 2 ml. of 1 N hydrochloric acid; (2) 2 ml. 3 N ammonium acetate; and (3) 2 ml. of reagent. The mixture was allowed to stand 5 minutes and (4) 2 ml. of 6 N ammonium hydroxide; and (5) 4 ml. of 6 N ammonium carbonate were added.

The results are given in Table 10:

TABLE 10.—REACTIONS OF ALUMINON WITH CATIONS

Ion	Aluminon	Ammonium Hydroxide	Ammonium Carbonate
As^{+3}	R soln.	Almost decolor. soln.	Decolor.
Cb^{+2}	Br-R ppt.	Ppt. dissv.-pale Y soln.	..
Dy^{+3}	R soln.	Purple soln.	..
Gd^{+3}	R ppt.	Ppt. dissv.-purple soln.	..
Hf^{+4}	Deep pink soln.	Light pink soln.	..
Ir^{+4}	R soln.	Pale Y soln.	Soln. almost color.
Mo^{+6}	R ppt.	Ppt. dissv.-pale Y soln.	.. .. ..
Pr	R ppt.	Ppt. dissv.-pink soln.	Decolor.
Re	R soln.	Pale Y soln.	Soln. almost color.
Rh^{+3}	Br-R ppt.	Ppt. dissv.-Y soln.	.. .. ..
Ru^{+3}	Pink soln.	Pale Y soln.	Dingy Y soln.
Sm^{+3}	R soln.	Pale purple soln.	Decolor.
Ta^{+5}	Br-R ppt.	Ppt. dissv.-pale Y soln.	Soln. almost color.
Te^{+6}	R soln.	Pale Y soln.	.. .. ..
Tm^{+6}	R soln.	Purple soln.	Decolor.
W^{+6}	Br-R ppt.	Ppt. dissv.-pale Y soln.	Soln. almost color.
UO_2^{+2}	R soln.	Pale Y soln.	.. .. ..
V^{+2}	Scarlet ppt. and soln.	Ppt. dissv.-pale pink soln.	Dissolves ppt.
Yb	Deep pink soln.	Pink soln.	Decolor.

Abbreviations: R = red: Y = yellow: Br = brown
Decolor. = decolorize: Dissv. = dissolves

If the concentration of aluminum exceeds 0.005-0.070 mg. of aluminum in 50 ml. of solution, the red lake may precipitate. Lampitt, Sylvester and Belham [40] suggest the use of glycerol to stabilize the lake, and Thrun [9] recommends gum arabic to prevent its precipitation. Gelatin has also been used.[37]

Detection of scandium. Scandium forms with aluminon a red lake resembling that of aluminum. It is insoluble in ammonium hydroxide, but dissolves in ammonium carbonate. This reaction has been used by Beck [27] as a microtest for scandium.

Detection of gallium. The gallium lake of aluminon resembles that of aluminum in appearance, but forms rather slowly. It is insoluble in ammonium hydroxide, but dissolves in ammonium carbonate after some time. Although this reaction has been used as a test for gallium, Wenger and Duckert [28] report that it is not sufficiently sensitive to be of great analytical value.

Determination of fluoride. An indirect method for the determination of fluoride in apatite or phosphorite has been proposed by Osherovich.[29,30]

Procedure. Dissolve 1 g. of material to be tested in sulfuric acid and distill into a receiver containing 1.5 g. potassium chloride, and add water to make the total volume 500 ml. To 10-20 ml. of this solution (0.06-0.14 mg. of fluoride) add 0.04 mg. of aluminum (as aluminum chloride), 5 ml. N hydrochloric acid, 5 ml. 3 N ammonium acetate, 5 ml. of 0.1 per cent aluminon and 0.5 ml. of 5 N ammonium carbonate. Finally add water to make 100 ml. After one hour compare the intensity of the coloration with that obtained with standard solutions prepared in a similar manner.

Detection of thorium. Hammett and Sottery [1] observed that aluminon reacts with thorium to give a color reaction, but this reaction is not recommended for the detection of thorium.[31]

1. L. P. Hammett and C. T. Sottery, *J. Am. Chem. Soc.* 47, 142-43 (1925); *C.A.* 19, 797 (1925).
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CITRIC ACID

$C_6H_8O_7$ Mol. Wt. 192.12 Beil. Ref. III, 556.

$$HO_2C—CH_2—(HO)C(CO_2H)—CH_2—CO_2H$$

Use: Detection of bismuth, hyponitrous acid, nitrite, oxygen, and water.

Determination of aluminum, copper, mercury, nickel, oxygen and thorium.

Citric acid consists of colorless, odorless, translucent crystals which possess a pleasant sour taste. The compound is obtained as the monohydrate. It becomes anhydrous on heating to 40-50° C. and is slightly deliquescent in moist air. The hydrate melts at about 100° C. when rapidly heated; the anhydrous acid melts at 153° C. One gram of the solid dissolves in 0.5 ml. of water, 1.8 ml. of alcohol, and 100 ml. of absolute ether.

Complex ion formation and buffer action. The most important use of citric acid in analytical chemistry is for the formation of soluble complexes with ions which otherwise would precipitate at low hydrogen ion concentrations. It is of great value in certain analytical procedures during the course of which it is essential that compounds of zinc, aluminum, iron, chromium, and copper remain in solution. For example, Schubert[1] used citric acid to eliminate complex forming metals in copper analysis, and Zen-Heo Pan[2] used this acid to eliminate interference by iron with the electrolytic determination of copper. Germuth[3] determined the affect of varying pH upon the formation of complex ions with citric acid and the pH of solutions containing sufficient citric acid to form complex ions with certain metals and thereby prevent their reaction with the usual chemical reagents. These results are shown in Table 11:

TABLE 11.—HYDROGEN ION CONCENTRATION OF SOLUTIONS OF CITRATE COMPLEXES

(Containing a slight excess of citric acid)

Metal	pH
Zinc	0.9-1.2
Chromium	1.4-1.6
Copper	1.2-1.4
Aluminum	4.5-4.8
Iron	0.6-0.8

These data show the hydrogen ion concentration of solutions of certain salts and citric acid at which complete solubility is most easily attained.

Curtmann and Dubin[13] have shown that 50 ml. of a solution containing 50 mg. of citric acid yields no precipitate of the hydrous oxide of iron, aluminum or chromium when treated with ammonium hydroxide unless there is present at least 40 mg. of aluminum, 70 mg. of iron and 90 mg. of chromium. The precipitation of aluminum by sodium phosphate is also hindered by citric acid, but not by tartaric acid.

Citric acid and the alkali salts of citric acid are very extensively used in analytical chemistry for the adjustment of pH in various procedures. For example, Golendeev[4] uses sodium citrate in a titrimetric procedure for the determination of nickel:

Procedure. Add 10 ml. of a 10 per cent aqueous solution of sodium citrate to 20 ml. of the solution containing nickel, and heat at 100° C. for 15-20 minutes. Cool, add 10 ml. of 10 per cent aqueous ammonia and dilute to 250 ml. Add 10 ml. of 0.04 N potassium cyanide to 20 ml. of this solution, and finally titrate the excess potassium cyanide with 0.02 N silver nitrate.

Citric acid is also used as a buffer in the detection of hyponitrous acid with resorcinol.[3]

Determination of mercury. Citric acid prevents the precipitation of small quantities of mercury by hydrogen sulfide. Under suitable conditions mercury is converted to a colored colloidal solution which is suitable for colorimetric comparison. Citric acid is added to the solution to be analyzed until the concentration is 1 per cent, and the mixture is saturated with hydrogen sulfide. The resulting color is compared with that of a standard solution containing 1 g. of mercuric chloride in 10,000 g. of water. Differences of concentration of 1 part in 100,000 can be detected by this method.[7]

Determination of aluminum. By the action of some salts on a mixture of an aluminum salt with an alkali metal tartrate, the acidity of the mixture increases markedly, and becomes equivalent to the amount of aluminum present in the solution. The aluminum content can be determined by titrating the acid formed with a base, using phenolphthalein as the indicator. If the tartrate is replaced with a citrate, the resulting acidity is equivalent to two-thirds of the aluminum content.[8] For the details of this procedure, see section on tartaric acid (page 180).

Determination of thorium. Thorium is precipitated from an acetone solution by citric acid. Cerium, lanthanum, praseodymium and neodymium are also precipitated. This reaction does not appear to show much promise as a qualitative procedure.[9]

Detection of bismuth. The formation of bismuth iodide-brucine complex serves as a particularly satisfactory reaction for the detection of bismuth. Brucine is much more soluble in a hot solution of citric acid than in water, and this reagent is much more suitable than solutions in alcohol, chloroform, acetic acid or hydrochloric acid. To prepare the reagent, dissolve 100 g. of citric acid in 100 ml. of water, add 12 g. of brucine and heat until solution is complete. For details of this test, see section on brucine.[14]

Detection of nitrite. Leclere [10] has suggested a modification of the ferrous sulfate reaction for the detection of nitrite in the presence of nitrate. This test depends on the fact that citric acid liberates nitrous acid from its salt without affecting nitrates:

Procedure. To the solution to be tested add an equal volume of a syrupy citric acid solution and mix well. Then carefully overlay with a solution of ferrous ammonium sulfate. A brown ring at the junction of the two liquids indicates the presence of nitrite.

Detection of water. Van Eck [11] has used Mann's [12] reagent for the detection of water in alcohol, ether and air. Mann's reagent is prepared as follows:

Reagent. Fuse together 2 g. of molybdic acid and 4 g. of citric acid, and dissolve the product in water. Impregnate filter paper with this solution and allow to dry. The blue color is decolorized by moisture.

Detection and determination of oxygen and oxidizing agents. The active oxygen in oxidizing agents may be determined by the orange color which is formed with citric acid and ammonium molybdate.[5] It is necessary that the solution of the material tested be colorless.

Procedure. Shake 10 g. of the sample with water that is heated to 50-60° in a 250-ml. graduated flask. Cool after 5 minutes, and treat carefully with an excess of a 20 per cent solution of citric acid. Dilute to the mark, add 1 g. of diatomaceous earth, mix well and filter. Place 5 ml. of the filtrate in a comparison tube, add 5 ml. of 20 per cent citric acid and 5 ml. of 10 per cent ammonium molybdate solution. Compare by dilution with a standard solution of sodium perborate which has been similarly treated. A permanent standard may be prepared by diluting a solution of potassium dichromate to match a developed standard solution of sodium perborate.

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2. Zen-Heo Pan, *Nanking J.* 2, 193-9 (1932); *C.A.* 29, 6528 (1935).
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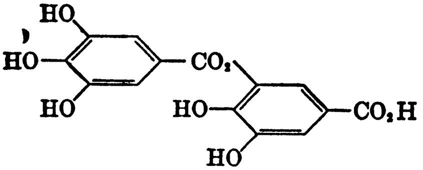
DIGALLIC ACID

$C_{14}H_{10}O_9$ Mol. Wt. 322.22 Beil. Ref. X, 486.



Use: Separation and determination of columbium, tantalum and tungsten. Digallic acid is an amorphous powder. It is easily soluble in water, alcohol, acetic acid, and acetone, but it is insoluble in chloroform. It melts below 100° C. with loss of water of hydration.

Preparation: Digallic acid is obtained by heating gallic acid and concentrated sulfuric acid on a water bath. The product is poured into cold water and shaken out with ethyl acetate.[1]

Reactions: Despite the many important uses of gallotannin (tannic acid) for the separation and determination of such metals as tungsten, columbium, and tantalum, the actual composition of individual samples of the reagent varies somewhat, and this suggests possible errors in the methods employing this compound. For this reason Nierenstein[2] suggests replacing gallotannin in analytical procedures with pure digallic acid. Schoeller,[3] however, has investigated the analytical possibilities of this reagent, and has found that a solution of oxalotantalic acid gives a yellow color with incomplete precipitation when treated with the reagent, and that a solution of oxalocolumbic acid yields a yellow color, but that precipitation is quite incomplete. According to Schoeller, it appears unlikely that digallic acid can ever replace gallotannin for the separation of tantalum and columbium.

An acid solution of sodium tungstate gives a dark brown precipitate with digallic acid.

1. C. Bottinger, *Ber.* 17, 1475 (1884).
2. M. Nierenstein, *Analyst.* 50, 604-5 (1925) ; *C.A.* 20, 1967 (1926).
3. W. R. Schoeller, *Analyst.* 52, 702 (1927) ; *C.A.* 22, 558 (1928).

DIHYDROXYMALEIC ACID

$C_4H_4O_6$ Mol. Wt. 148.07 Beil. Ref. III, 540.

$$HO_2C—C(OH)=C(OH)—CO_2H$$

Use: Detection of titanium and fluorides.

Dihydroxymaleic acid crystallizes from water as plates with two moles of water. The anhydrous compound decomposes at 155° C. without melting. The reagent is very slightly soluble in cold water, ether, and acetic acid, but it is more soluble in methyl alcohol and ethyl alcohol.

Preparation: Boil a hot saturated aqueous solution containing 250 g. of tartaric acid with 1 g. of powdered iron (*ferrum reductum*) until the iron has dissolved. Filter and cool the mixture to 0° C., and then gradually add 20 per cent by volume or stronger, hydrogen peroxide in small portions until the color of the solution remains dark green for 2-3 minutes. Then add gradually a quantity of fuming sulfuric acid equal to 0.1 the total volume of the solution. Allow to stand at 0° C., and after a few days filter off the separated crystals.[1,2]

Detection of titanium and fluoride: When dihydroxymaleic acid is added to a cold dilute aqueous solution containing salts of tetravalent titanium, an intensely colored reddish-brown solution is obtained. This color is immediately discharged by the addition of hydrogen fluoride or a soluble fluoride; hence, this reaction may be employed to detect both titanium and fluorides. The reaction is said to be particularly useful for detecting traces of titanium, since it is more sensitive than the hydrogen peroxide test, and may be made in the presence of vanadium.

A voluminous chocolate-colored precipitate, having the composition of $C_4H_4O_6 \cdot 2TiO_2 \cdot 2.5H_2O$ separates when the reagent is added to more concentrated solutions of titanium salts.[3]

When hydrogen peroxide is added to a solution containing titanium and vanadium, a red color is obtained with both metals. If dihydroxymaleic acid is used instead of the peroxide, however, a color is obtained only with titanium. By measuring in a tintometer the colors produced with both reagents, and preparing curves showing the relation of concentration of the metal to the color of the solution, it is possible to determine titanium and vanadium in the presence of one another. By comparing the effect produced by hydrogen peroxide on a solution containing both titanium and vanadium, and the effect produced by dihydroxymaleic acid on another portion of the same solution, the concentration of the two metals may be read from the curve.[4]

1. H. J. H. Fenton, *J. Chem. Soc.* **65**, 901 (1894).
2. H. J. H. Fenton, *J. Chem. Soc.* **87**, 811 (1905).
3. H. J. H. Fenton, *Proc. Chem. Soc.* **24**, 133 (1908); *C.A.* **2**, 2200 (1908).
4. J. W. Mellor, *Trans. Ceram. Soc. England.* **12**, 33 (1913).

DIHYDROXYTARTARIC ACID

Synonym: Diketosuccinic acid

$C_4H_6O_8$ Mol. Wt. 182.09 Beil. Ref. III, 830(288).

$$HO_2C—(HO)_2C—C(OH)_2—CO_2H$$

Use: Detection of sodium.

Dihydroxytartaric acid is a white crystalline powder. It melts at 114-115° C. with decomposition. It is very soluble in water, but the aqueous solution decomposes on heating.

Preparation: *Tartaric acid dinitrate:* Add 10 g. of finely divided tartaric acid to a mixture of 30 g. nitric acid ($d = 1.52$) and 8 g. of phosphorus pentoxide, and allow the mixture to stand for about one-half day with cooling. Filter through glass wool, using suction. Shake a small portion of the mixture with a little ether and ice. Draw off the water which is formed and add alternately fresh portions of ice and the nitrate. Finally, wash the ether solution with ice water and evaporate in a desiccator.[1]

Dihydroxytartaric acid. Dissolve the crude dried tartaric acid dinitrate in a little cold water, and neutralize the greater part of the acid with solid sodium carbonate until the color of malachite green paper is no longer changed, and then mix with a saturated solution of sodium acetate. Allow the mixture to stand for 24 hours. The sodium salt of dihydroxytartaric acid which separates is converted to the free acid by decomposing with hydrogen chloride gas under absolute ether, avoiding an excess.[2]

Detection of sodium. Dihydroxytartaric acid produces a yellow insoluble precipitate when added to solutions of sodium salts. This reaction may be used for the detection of sodium.[3,4] The presence of ammonium and potassium salts does not interfere with this reaction.

1. R. Behrend and H. Osten, Ann. **343**, 153 (1905).
2. W. L. Miller, *Ber.* **22**, 2016 (1889).
3. H. J. H. Fenton, *J. Chem. Soc.* **65**, 899 (1894).
4. J. V. Dubsky and M. Novakova, *Chem. Obzor.* **15**, 136-9 (1940); *C.A.* **37**, 49 (1943).

GLUCONIC ACID

Synonym: Dextronic acid, *d*-glyconic acid

$C_6H_{12}O_7$ Mol. Wt. 196.16 Beil. Ref. III, 542

$$CH_2OH—CHOH—CHOH—CHOH—CHOH—CO_2H$$

Use: Determination of aluminum.

Gluconic acid is a nearly colorless, syrupy liquid. It has a mild acid taste and is miscible with water. At ordinary temperatures or upon evaporation of its aqueous solution, gluconic acid is largely transformed into a lactone, which is a white solid.

Preparation: Dissolve 50 g. of glucose in 400 ml. of water, and treat in a stoppered bottle with 100 g. of bromine. Allow to stand for 3 days at room temperature with frequent shaking. Boil with constant stirring until all bromine is expelled. Cool and dilute to 500 ml. Neutralize with lead carbonate suspended in water. Filter with suction, suspend the precipitate in water and saturate with hydrogen sulfide. Filter and neutralize the filtrate by boiling 30 minutes with precipitated chalk. Evaporate the filtrate to about 100 ml. and seed in the cold with crystals of calcium gluconate. Allow to stand 24 hours, and filter with suction. Wash the precipitate with cold water, redissolve in a small quantity of hot water, and boil with a little decolorizing charcoal. Filter off the charcoal, and treat the filtrate with the exact quantity of oxalic acid (in aqueous solution) necessary to precipitate all calcium. Filter off the calcium oxalate and wash, and evaporate the washings and filtrate to a syrup on a warm water bath under reduced pressure.[1]

Determination of aluminum. Aluminum sulfate reacts with gluconic acid or its salts by the replacement by aluminum of the hydrogen of the hydroxyl groups and the liberation of sulfuric acid. The latter may be titrated with sodium hydroxide, using phenolphthalein as the indicator. The reaction is quantitative only when carried out at 100° C.[2]

1. H. Kiliani and S. Kleemann, *Ber.* **17**, 1298 (1884).
2. A. V. Pavlinova, *Acta Univ. Voronegiensis.* 9, No. 3, 59-68 (1937); *C.A.* **32**, 6970 (1938).

GLYCERIC ACID

$C_3H_6O_4$ Mol. Wt. 106.08 Beil. Ref. III, 392

$$CH_2(OH)—CH(OH)—CO_2H$$

Use: Determination of aluminum.

Glyceric acid is a thick syrupy liquid which is miscible with alcohol and water, but which is insoluble in ether.

Preparation: Mix 50 g. of glycerol in a tall, narrow glass cylinder with an equal volume of water, and by means of a long thistle tube, underlay with 50 g. of red, fuming nitric acid. Allow to stand for 3 or 4 days and evaporate the contents of 3 such tubes on a water-bath slowly to about 270 g. Allow to stand for a time during which a slow evolution of gas occurs, and then mix in a dish with 1800 ml. of water. Gradually add 400 g. of lead carbonate and allow to stand for 24 hours. Warm with stirring to 61-65° C. and maintain at this temperature for 2 hours. Decant off the liquid and allow to crystallize and then add the mother liquor to the solid mass. Replace the evaporated water and repeat the above operation two more times. Dissolve the colorless lead glycerate in hot water and precipitate lead by treating with hydrogen sulfide. Filter and evaporate to obtain glyceric acid.[1]

Determination of aluminum. Aluminum sulfate reacts with glyceric acid and its salts due to the replacement by aluminum of the hydrogen of the hydroxyl groups. This reaction is accompanied by the liberation of an equivalent quantity of sulfuric acid, which may be titrated with sodium hydroxide and phenolphthalein. The reaction is quantitative only if carried out at 100° C.[2]

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1. E. Mulder, *Ber.* **9**, 1902 (1876).
2. A. V. Pavlinova, *Acta Univ. Voronegiensis.* **9**, 59-68 (1937); *C.A.* **32**, 6970 (1938).

1-HYDROXY-2-NAPHTHOIC ACID

$C_{11}H_8O_3$ Mol. Wt. 188.17 Beil. Ref. X, 331

$$HO—C_{10}H_6—CO_2H$$

Use: Detection of ammonium, magnesium and potassium.

1-Hydroxy-2-naphthoic acid is a crystalline solid melting at 185-186° C. It is only very slightly soluble in water, but dissolves readily in alcohol, ether and benzene.

Detection of potassium, ammonium and magnesium. Rosenthaler[1] reports that 1-hydroxy-2-naphthoic acid yields characteristic microcrystals with potassium, ammonium and magnesium salts.

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1. L. Roenthaler, *Mikrochemie.* **2**, 29 (1924); *C.A.* **18**, 2481 (1924).

LACTIC ACID

Synonym: α-Hydroxypropionic acid

$C_3H_6O_3$ Mol. Wt. 90.08 Beil. Ref. III, 268

$$CH_3—CH(OH)—CO_2H$$

Use: Determination of copper and zinc.

Lactic acid is a colorless syrupy liquid. It has a sp. gr. of 1.206. It is miscible with water, alcohol and glycerol. It is also freely soluble in ether but insoluble in chloroform. When lactic acid is concentrated above 50 per cent, it is partially converted into lactic anhydride. For this reason the U.S.P. commercial product usually contains about 15 per cent of the anhydride.

Determination of copper and zinc. Interference of iron with the electrolytic determination of copper is eliminated by the addition of lactic acid.[1] Zinc may also be separated electrolytically in the presence of manganese from a lactic acid solution.[2]

1. Zen-Heo Pan, *Nanking J.* 2, 193-9 (1932); *C.A.* 29, 6528 (1935).
2. E. J. Riederer, *J. Am. Chem. Soc.* 21, 789 (1899).

MALIC ACID

Synonym: *l*-malic acid

$C_4H_6O_5$ Mol. Wt. 134.09 Beil. Ref. III, 417

$$HO_2C—CH_2—CH(OH)—CO_2H$$

Use: Alkalimetric standard.

Malic acid occurs in the juice of apples and many fruits and may be prepared by the catalytic hydration of maleic acid. It is a white crystalline solid melting at 99-100° C. It boils at about 140° C. with decomposition. It is readily soluble in water but only slightly soluble in alcohol, ether and methyl alcohol.

Preparation: Dissolve 25 g. of asparagine in 50 ml. of dilute nitric acid, and pass the oxides of nitrogen into this mixture for 7 hours, while the solution is heated on a steam bath. After the evolution of nitrogen has ceased, neutralize the solution with potassium hydroxide and add lead acetate. Collect the precipitate, wash with warm water, suspend in water, and decompose with hydrogen sulfide. Filter off the lead sulfide, and concentrate the filtrate to a syrup on a steam bath. Dissolve the residue in acetone and filter, and remove the acetone by distilling *in vacuo*. Crystallize the residue.[1]

Standardization of sodium hydroxide. Lange and Kline[2] have studied the use of malic acid for the standardization of sodium hydroxide solutions. They report that results are as accurate as those obtained by standardizing hydrochloric acid solutions as silver chloride. Since malic acid is very soluble in water, it is purified by dissolving in hot acetone, filtering, and adding carbon tetrachloride to the hot solution. On cooling, the pure crystalline solid separates. The crystals are dried in air for 24 hours and then in a desiccator over sulfuric acid for 24 hours. The reagent cannot be used with ammonium hydroxide solutions and it cannot be used in iodometric titrations.

1. P. Walden, *Ber.* 28, 2771 (1895).
2. N. A. Lange and H. Kline, *J. Am. Chem. Soc.* 44, 2709-12 (1922); *C.A.* 17, 506 (1923).

MANDELIC ACID

Synonym: α-Hydroxyphenylacetic acid, phenylglycolic acid.

$C_8H_8O_3$ Mol. Wt. 152.14 Beil. Ref. X, 197

$$C_6H_5—CH(OH)—CO_2H$$

Use: Detection of copper.

Mandelic acid is a white crystalline solid which possesses a faint odor. It melts at 117-118° C. One gram of the solid dissolves in 6.3 ml. of water and 1 ml. of alcohol, but is freely soluble in ether and isopropyl alcohol.

Preparation: *Dichloroacetophenone.* Fit a 3-liter flask with a 3-hole rubber stopper, through which is passed an inlet tube extending to the bottom of the flask, and outlet tube, and a thermometer. Connect the inlet tube to a cylinder of chlorine through a bubble counter consisting of a 500-ml. wash bottle containing 200 ml. of concentrated sulfuric acid. Connect the outlet tube to a gas absorption apparatus in which hydrogen chloride is absorbed by running water.

In the flask place 240 g. of acetophenone and 1 liter of glacial acetic acid. Adjust the thermometer so that the bulb extends considerably below the surface of the liquid, and pass in chlorine at such rate that the temperature does not exceed 60° C. Continue the chlorination until an excess of the halogen has been absorbed. This requires about 5 hours. Completion of the chlorination is indicated by a yellow color. Pour the mixture over 5-6 liters of crushed ice. Stir several times, and allow to stand until the ice is melted. Dichloroacetophenone separates as an oil and is recovered (lachrymator).

Mandelic acid. In a 2-liter, 3-necked flask, which is fitted with a stirrer, dropping funnel and a thermometer, place 156 g. of sodium hydroxide dissolved in 1.4 liters of water. Warm to 60° C. and stir vigorously, and while stirring add 200 g. of dichloroacetophenone from the dropping funnel. Add slowly at first so that the temperature does not exceed 65° C. This operation requires about 2 hours. Stir an additional hour, while still keeping the temperature at 65° C. Add 170 ml. of 12 N hydrochloric acid and extract with ether. Use about 250-300 ml. of ether, and carry out the extraction in a continuous extractor. Transfer the ether extracts to a 1-liter flask, and remove the ether by distillation.

Dry the residue of crude mandelic acid by warming on a steam bath under the vacuum of a water pump. Add 400 ml. of benzene and distill until 100 ml. of benzene has passed over. Then add 6-10 ml. of ethyl alcohol to the residue in the flask to bring the acid completely into solution. Filter the hot solution through a warm Buchner funnel, and cool the filtrate overnight at 6° C. Collect the crystals of mandelic acid, and evaporate the filtrate to one-fourth its volume to recover an additional quantity of the acid.[1,2]

Detection of copper. Mandelic acid or its ammonium salt reacts with copper to give a greenish-white precipitate. This reaction may be used for the detection of copper:[3]

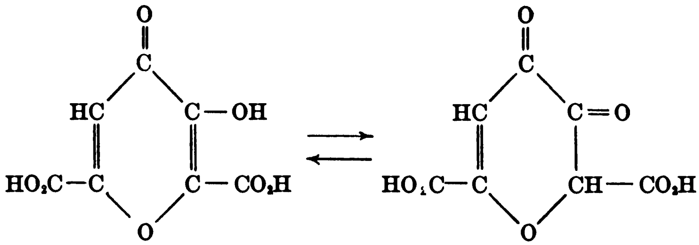
Procedure. To 2-3 ml. of the copper solution in a test tube, add 8-10 drops of a 10 per cent solution of ammonium mandelate or mandelic acid and boil for about 30 seconds. A slight greenish-white precipitate forms if copper is present. This reaction is sensitive to 0.2 mg. of copper.

The precipitate formed with mandelic acid consists of hexagonal plates, while the ammonium salts yield spherodial masses or crystals.

1. L. Gattermann and H. Wieland, *Laboratory Methods of Organic Chemistry,* Translated from 24th German ed., pp. 227-8, Macmillan, London (1941).
2. *Organic Synthesis,* Collective Vol. I, 2nd ed., p. 336. John Wiley, New York (1941).
3. G. Deniges, *Bull. trav. soc. pharm. Bordeaux.* 77, 148-9 (1939) ; *C.A.* 34, 7204 (1940).

MECONIC ACID

$C_7H_4O_7 \cdot 3H_2O$ Mol. Wt. 254.15 Beil. Ref. XVIII, 503



Use: Detection of iron and vanadium chloride.

Meconic acid, a substance obtained from opium, consists of white lustrous crystals, which become anhydrous at 100° C. The compound decomposes at a higher temperature. It is slightly soluble in cold water and absolute ether; it is soluble in about five parts of boiling water; and is soluble in alcohol and benzene.

Preparation: Extract opium with luke-warm water, treat the neutral solution with calcium chloride, boil for a few minutes, and dilute with water. The calcium salt which separates is converted to meconic acid by treating with a mixture of 20 parts of boiling water and 3 parts of concentrated hydrochloric acid.[1,2]

Detection of iron and vanadium chloride. As little as 0.1 g. of vanadium chloride in 1 liter of solution gives a red color with a hot aqueous solution of meconic acid. If the reagent is carefully poured onto the surface of the solution of vanadium chloride, but is not mixed with the latter, the red color is obtained at the zone of contact of the two liquids. Hydrochloric and sulfuric acids do not interfere, but oxalic acid and metaphosphoric acid must be absent. Meconic acid reacts with ferric chloride in the presence of hydrochloric acid to give a red color.[3]

1. Dr. Gregory, *Ann.* **24**, 43 (1837).
2. H. How, *Ann.* **83**, 351 (1852).
3. K. Woynoff, *Ber.* **67B**, 54 (1934) ; *C.A.* **28**, 3686 (1934).

PROTOCATECHUIC ACID

Synonym: 3,4-dihydroxybenzoic acid

$C_7H_6O_4$ Mol. Wt. 172.13 Beil. Ref. X, 389

$$(HO)_2C_6H_3—CO_2H$$

Use: Detection of iron.

Protocatechuic acid is a white to brownish crystalline powder, which becomes discolored in air. It melts at 194° C. with decomposition. It dissolves in 50 parts of water but is soluble in alcohol and ether.

Preparation: Protocatechuic acid is prepared by heating 1 part of pyrocatechol with 4 parts of ammonium carbonate and 5 parts of water for 16 hours in a closed tube at 130-140° C. To recover the compound, cool and neutralize the mixture with hydrochloric acid, and extract the unchanged pyrocatechol with ether. Mix the aqueous solution with an excess of hydrochloric acid, and with repeated extractions of ether remove the acid. The compound is obtained as a brown crystalline solid by evaporating the ether. Crystallize from hot water.[1]

Detection of iron. Iron may be detected by the red coloration which appears when protocatechuic acid is added to a slightly acid solution containing ferrous or ferric salts, and then made alkaline with a slight excess of normal sodium carbonate.[2,3]

If a colored precipitate is formed on the addition of sodium carbonate, it is best to filter the solution and observe the color of the filtrate. The sensitivity of this reaction is 1:10,000,000.

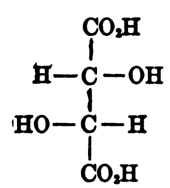
The principal advantage of this reaction lies in the fact that the presence of other compounds such as mercuric chloride, arsenic acid, phosphoric acid and many organic acids does not diminish its sensitivity. In the presence of strong acids or strong alkalis, however, no color is produced.

1. A. K. Miller, *Ann.* 220, 116.
2. O. Lutz, *Chem.-Ztg.* 31, 570 (1907); *C.A.* 2, 242 (1908).
3. H. Fritz, *Z. anal. Chem.* 78, 418-27 (1929); *C.A.* 24, 310 (1930).

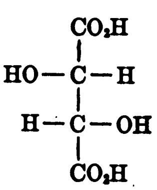
RACEMIC ACID

Synonym: *dl*-Racemic acid, uvic acid, paratartaric acid

$C_4H_6O_6$ Mol. Wt. 150.09 Beil. Ref. III, 522



and



Use: Detection of calcium and potassium.

Determination of calcium and strontium.

Racemic acid appears as white, triclinic crystals. This is not simply an equimolecular mixture of *d*- and *l*-tartaric acids, but a compound of the two formed by secondary valences. The compound has a specific gravity of 1.7, and melts at 203-204° C. ((206° when anhydrous). It crystallizes with 1 or 2 moles of water below 73° C. It is anhydrous above this temperature. One g. of racemic acid dissolves in 5 ml. of cold water, 0.5 ml. of boiling water, 65 ml. of alcohol and 140 ml. of ether.

Preparation: Dissolve 360 g. of *d*-tartaric acid in 2 liters of 4 N sodium hydroxide. Boil gently in a copper flask under reflux for one week. Make distinctly acid with concentrated hydrochloric acid and evaporate to 500 ml. Filter while hot and to the filtrate add 200 ml. of concentrated hydrochloric acid. Again filter, add 1 liter of 95 per cent alcohol and filter again. Distill the alcohol from a steam bath, and allow the residue to evaporate from an open dish on a steam bath until the volume of liquid is 150 ml. Add a few crystals of racemic acid and allow the mixture to stand 24 hours. Mascerate the residue with 100 ml. of cold water and filter. Dissolve the crude racemic acid in hot water, boil with animal charcoal, filter, and allow to crystallize. Dry in an oven at 80° C., and again recrystallize from water.[1]

Detection of potassium. Racemic acid may be substituted for *d*-tartaric acid in the well-known test for potassium, which depends upon the formation of potassium acid tartrate. According to Szebelledy and Jonas,[2] racemic acid is superior to *d*-tartaric acid; because, for some unknown reason, the potassium hydrogen tartrate formed with racemic acid does not show as much tendency to form a supersaturated solution as that with *d*-tartaric acid. Consequently, it is not necessary to scratch the glass walls of the vessel.

Determination of calcium and strontium. Calcium and strontium racemates precipitate quite rapidly when solutions of calcium and strontium salts are treated with a 10 per cent solution of racemic acid. This occurs even when the concentration of strontium is as low as 1:10,000 and calcium 1:500,000. Barium racemate precipitates in the cold only after several hours, although the presence of barium diminishes the sensitivity of the strontium and calcium reactions. Calcium and strontium cannot be determined in the presence of barium, because of the difficulty in removing all of the latter, even by repeated precipitations. Calcium is determined with the aid of racemic acid according to the method of Kling.[3]

Procedure. Dilute a solution containing 0.2-0.3 g. of calcium to 100 ml., add 10 ml. of a solution containing 10 per cent acetic acid and 10 per cent sodium acetate, and then add 10-20 ml. of a 10 per cent solution of racemic acid. Calcium is completely precipitated within 30 minutes. Filter and wash the residue with cold water. The residue may be dissolved in sulfuric acid and titrated with potassium permanganate, or it may be ignited and weighed as calcium oxide.

Strontium may be determined by using the above procedure, but the results are less accurate than those obtained with calcium.

1. A. N. Campbell, L. Slotin, and S. A. Johnston, *J. Am. Chem. Soc.* **55**, 2604 (1933).
2. L. Szebelledy and J. Jonas, *Z. anal. Chem.* **107**, 114-16 (1936); *C.A.* 31, 627 (1937).
3. A. Kling, *Bull. soc. chim.* **9**, 355-61 (1911); *C.A.* **5**, 2381 (1911).

β-RESORCYLIC ACID

Synonym: 2,4-Dihydroxybenzoic acid

$C_7H_6O_3$ Mol. Wt. 154.12 Beil. Ref. X, *377*

$(HO)_2C_6H_3—CO_2H$

Use: **Detection of titanium and uranium.**

Determination of iron and uranium.

β-Resorcylic acid melts at 216-217° C. with decomposition. It is soluble in 381 parts of water, and is easily soluble in warm water, alcohol, and ether.

Preparation: Mix 200 g. of resorcinol, 1000 g. of potassium bicarbonate and 2000 ml. of water in a 5-liter flask. Fit the flask with a reflux condenser, and heat the mixture slowly on a water bath for 4 hours. Then heat over a free flame and boil vigorously for 30 minutes while passing a rapid stream of carbon dioxide through the mixture. While still hot, acidify with 900 ml. of concentrated hydrochloric acid, which is added from a separatory funnel with the stem delivering acid to the bottom of the flask to prevent the formation of an acid layer on the surface of the liquid. Allow the mixture to cool to room temperature, and then chill.

Filter the crude acid, and recover an additional quantity of the product by extracting the filtrate several times with ether. Shake the ether extracts with an aqueous solution of sodium bicarbonate to recover the resorcylic acid. Acidify the aqueous solution with hydrochloric acid, and again extract with ether. Evaporate the ether, and recrystallize the colored product several times from boiling water containing charcoal.

Combine the two portions of crude acid, and dissolve in 1000 ml. of water. Boil with 25 g. of Norite, filter through a heated filter, and crystallize by cooling in an ice-salt freezing mixture while stirring vigorously.[1,5]

Detection and determination of uranium. Resorcylic acid may be used to replace gallic acid for the detection and colorimetric determination of uranium.

Detection of titanium. Solutions of titanium salts containing 1 mg. of the element per ml. give a faint yellow coloration with resorcylic acid.[3]

Determination of iron. Resorcylic acid forms a red complex with ferric ions. This appears to be stable in sunlight and on standing. Color standards are prepared as follows:[4]

Procedure. Place suitable volumes of standard iron solutions in 100-ml. Nessler tubes, and add 25 ml. of a buffer solution consisting of 1 part of 1 N hydrochloric acid and 1 part of 1 N sodium acetate, and finally add 1 ml. of a saturated solution of resorcylic acid (0.017 M). Dilute to the mark and compare the color with that of unknown solutions similarly prepared. The pH of the solution is 2.9. The most suitable pH appears to be 2.5-3.0.

Iron can be detected at a dilution of 1:20,000,000. Several salts interfere, but these have not been fully investigated.

1. A. Bistrzychi and St. v. Kostanecki, *Ber.* **18**, 1985 (1885).
2. P. N. Das-Gupta, *J. Indian Chem. Soc.* **6**, 763-76 (1929); *C.A.* **24**, 1212-13 (1930).
3. P. N. Das-Gupta, *J. Ind. Chem. Soc.* **6**, 855-63 (1929); *C.A.* **24**, 1820 (1930).
4. J. L. Larner and Wm. E. Trout, Jr., *Va. J. Sci.* **3**, No. 1, **13** (1942); *C.A.* **36**, 3114 (1942).
5. *Organic Synthesis,* **10**, 94-95 (1930).

SACCHARIC ACID (CALCIUM SALT)

Synonym: Calcium sacchrate

$C_6H_{10}O_8$ Mol. Wt. 210.14 Beil. Ref. III, 577

$HO_2C—(CHOH)_4—CO_2H$

Use: Detection of magnesium.

Calcium sacchrate is a white solid. It dissolves in about 12 parts of water but is insoluble in alcohol. The aqueous solution is strongly alkaline.

Preparation: Saccharic acid is prepared as follows: Mix 50 g. of anhydrous glucose with 350 g. of nitric acid (d = 1.15) and heat on a water-bath with constant stirring until a syrupy residue is obtained. Dissolve in a little water and again evaporate until the mass begins to turn brown. Interrupt the heating and dissolve the mixture in 150 ml. of water. Neutralize with a concentrated solution of potassium carbonate, and add 25 ml. of 50 per cent acetic acid. Concentrate to about 80 ml. Allow to stand until the potassium salt is crystallized. Rub the sides of the vessel, if necessary, to hasten crystallization. After standing for 12 hours, filter with suction, wash with a little cold water and recrystallize from the smallest possible quantity of hot water containing a little animal charcoal. The calcium salt is obtained by neutralizing with calcium hydroxide.[1]

Detection of magnesium. Calcium sacchrate is used for the detection of magnesium in the presence of barium, strontium and calcium:[2]

Procedure. Heat the sample in a test tube to 60-70° C. and add an excess of a 5 per cent calcium sacchrate solution. Shake vigorously. A white flaky precipitate forms if magnesium is present. This test is sensitive to 0.2 mg. of magnesium in 5 ml. of solution.

Magnesium is detected in a mixture of calcium, strontium, barium and ammonium salts by using a 10 per cent calcium sacchrate solution after removing ammonium salts with formaldehyde. This test is sensitive to 1.2 mg. of magnesium in 5 ml. of solution.

1. E. Fischer, *Anleitung z. Darstellung org. Praparate*, p. 80.
2. N. A. Tananaev and R. A. Lovi, *J. Applied Chem.* (*U.S.S.R.*). 10, 1112-17 (1937); *C.A.* 32, 1604 (1938).

SALICYLIC ACID

Synonym: o-Hydroxybenzoic acid

$C_7H_6O_3$ Mol. Wt. 138.12 Beil. Ref. X, 43

$HO—C_6H_4—CO_2H$

Use: Detection of aluminum, boron, cerium, copper, hyposulfite, iron, lead, manganese, mercury, nickel, nitrate, nitrite, silver, titanium, tungsten and vanadium.

Determination of aluminum, copper, iron, thorium, titanium, and uranium.

Alkalimetric standard and iodometric standard.

Salicylic acid consists of white odorless crystals which gradually become discolored in sunlight. The compound melts at 157-159° C., and sublimes at 76° C. When rapidly heated at ordinary atmospheric pressure it decomposes into phenol and carbon dioxide. One gram of the solid dissolves in 460 ml. of water, 15 ml. of boiling water, 2.7 ml. of alcohol, 3 ml. of acetone, 42 ml. of chloroform, 3 ml. of ether and 135 ml. of benzene.

Detection and determination of iron. An amethyst color is formed when salicylic acid or salts of salicylic acid are added to solutions of ferric salts. This reaction appears first to have been observed by Vogel,[1] and has since been reported by other investigators.[2-5] It was first used by Gregory [6,7] for the colorimetric determination of small quantities of iron in copper alloys. The depth of the red color is increased by using a solution of salicylic acid and carrying out the reaction in the presence of sodium acetate. The interfering blue color, caused by copper salts, may be removed by the addition of a dilute solution of potassium cyanide. Lead must be removed by precipitation as lead sulfate, but zinc and antimony do not interfere. The method of Gregory has more recently been developed and further applied by many workers and some of the limitations of the method have been observed.[8-13,65]

The following procedure has been proposed by Yoe: [15]

Reagents. *Salicylic acid:* A saturated solution is used.

Standard iron solution. Dissolve 0.0864 g. of ferric ammonium alum, $Fe_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$, in distilled water containing 2 ml. of concentrated sulfuric acid and dilute to 1 liter. One ml. of this solution contains 0.00001 g. of iron.

Procedure. To 20 ml. of a solution containng 0.01-0.2 mg. of iron, add 5 ml. of the salicylic acid solution and compare immediately with the color produced by adding 5 ml. of the reagent to 20 ml. of standard iron solution. Comparison may be made either by balancing or by the method of dilution.

Since ferrous iron does not give a color reaction with salicylic acid, only ferric iron is determined by the above procedure. Total iron may, however, be determined by first oxidizing ferrous iron by means of potassium permanganate:

Procedure. Acidify 20 ml. of the solution containing 0.01-0.2 mg. of iron with sulfuric acid and oxidize the ferrous iron with potassium permanganate. Neutralize the free acid with ammonium hydroxide, add 5 ml. of a saturated solution of salicylic acid, and match the color immediately with that of a standard to which has just been added 5 ml. of saturated salicylic acid solution.

The quantity of iron present in the solution to be analyzed must not exceed 0.2 mg., since the color produced by quantities greater than this is too intense for colorimetric comparison. Similarly, the color is too pale for a microchemical comparison if less than 0.01 mg. of iron is present. Phosphate, thiosulfate, sulfide, bisulfite, fluoride, free mineral acids, and citric and tartaric acids [9,15] interfere with this determination. If it is necessary to use acid to dissolve the sample, or to add an acid for the oxidation of ferrous iron with permanganate (for determination of total iron), the excess acid must be neutralized with ammonia before the addition of salicylic acid. In neutralizing excess acids with ammonia, care must be taken that ammonia is not added in excess. Should this occur, with the consequent precipitation of iron hydroxide, make the solution slightly acid and then add dropwise dilute ammonium hydroxide until the neutral point is just reached. For the determination of iron in organic matter, it is necessary to evaporate the sample to dryness with nitric acid, ignite, and dissolve the residue in water or dilute hydrochloric acid.

The color produced by the addition of salicylic acid to a solution of a ferric salt fades fairly rapidly in sunlight, and for this reason it is important that the standard and unknown be prepared simultaneously. Because of the rapid fading of the color, comparison of the unknown with a series of standards is not recommended. There is some difference of opinion as to the stability of the color produced by ferric ions and salicylic acid. As stated above, Yoe [15] claims that it fades rapidly in light, while Snell [10] says that the color is stable for 48 hours but that it fades rapidly in sunlight.

Scott [17] has studied the various methods for the colorimetric determination of iron and claims that the thiocyanate method is unsatisfactory for use with a photoelectric absorption meter while the reaction of ferric ion in acetic acid solution with sodium salicylate gives accurate and consistent results. The following prcoedure is recommended:

Procedure. Treat the iron solution containing the equivalent of 0.05-0.55 mg. Fe_2O_3 with 4 ml. of 6 N hydrochloric acid, 5 ml. of 1 per cent sodium salicylate solution and sufficient 7.5 N ammonium hydroxide to cause the amethyst color to turn yellow. Add 2 more drops of the ammonium hydroxide solution, and then add 50 per cent acetic acid dropwise to the appearance of a pink color, and 5 ml. in excess. Dilute to 50 ml. and measure in a photoelectric absorption meter.

Results obtained by the above procedure are reproducible to within 1 per cent.

Both ferrous and ferric ions give the same color in this test, which serves for the determination of total iron. Satisfactory results are obtained in the presence of 0.3 mg. of titanium, 3.5 mg. of aluminum, 12 mg. of manganese, 3.0 mg. of silica, 4.0 mg. of phosphate, 0.1 mg. of fluoride, and 2.0 mg. of chlorine.

TABLE 12.—EFFECT OF COMMON CATIONS UPON THE COLOR DEVELOPED BY IRON AND SALICYLIC ACID

(A solution of 0.5 mg. of iron in 100 ml. is used)

Cation	Concentration mg/100 ml.	pH	Apparent Change in the Iron Concentration in Per Cent
Aluminum	50	3.0	—26.2
Aluminum	10	2.7	—3.0
Ammonium	250	2.6	negative
Antimony	10	—	precipitates
Antimony	2	2.6	negative
Barium	50	2.7	+3.4
Barium	5	2.6	+1.2
Beryllium	50	3.1	—10.0
Beryllium	25	2.9	—1.8
Bismuth	10	—	turbidity
Bismuth	2	2.6	+20
Cadmium	200	2.4	negative
Calcium	50	2.6	negative
Chromic	2.5	2.7	change in hue
Cobalt	50	2.6	change in hue
Cobalt	5	2.6	+3.0
Copper	5	2.7	change in hue
Copper	1	2.6	negative
Lead	100	3.0	negative
Lithium	150	2.6	negative
Magnesium	100	2.6	negative
Manganese	50	2.6	slight change in hue
Mercuric	10	—	precipitates
Mercurous	2	—	slight turbidity
Nickel	10	2.6	change in hue
Nickel	2	2.6	negative
Potassium	250	2.6	negative
Silver	50	—	precipitates
Silver	30	2.7	negative
Sodium	260	2.6	negative
Stannic	10	—	precipitates
Stannous	10	2.7	turbidity
Stannous	5	2.7	slow fading
Strontium	50	2.6	negative
Thorium	50	2.6	+7.8
Thorium	10	2.6	negative
Uranyl	25(U)	2.6	change in hue
Uranyl	10(U)	2.6	change in hue
Zinc	50	2.7	negative
Zirconium	1	—	precipitates

The above method can be used for the analysis of soils and clays, and is particularly useful when 5-10 mg. of material is available and the iron content is 2-20 per cent.

Recently Mehlig[13,14] has studied the salicylic acid method for determining ferric iron, and by means of a recording photoelectric spectrophotometer has shown that the color produced with ferric iron and salicylic acid can be used advantageously for a colorimetric determination if the pH range is 2.6-2.8, and 1 ml. of the solution is mixed with 12 ml. of 50 per cent acetic acid by volume. According to these studies the color is stable in diffused light for 66 hours.

Mehlig[14] has exhaustively studied the effect of both anions and cations upon the accuracy of the iron determination by the salicylic acid method. His results are given in Tables 12 and 13.

TABLE 13.—EFFECT OF ANIONS UPON THE COLOR DEVELOPED BY IRON AND SALICYLIC ACID

(A solution of 0.5 mg. of iron in 100 ml. is used)

Anion	Concentration mg/100 ml.	pH	Apparent Change in the Iron Concentration in Per Cent
Arsenate	50 (As)	2.7	—43.4
Arsenate	10 (As)	2.6	—2.4
Arsenite	50 (As)	2.6	negative
Borate	150 (B_2O_3)	2.5	negative
Bromide	200	2.6	negative
Carbonate	200	2.8	negative
Chlorate	200	2.7	negative
Chloride	250	2.6	negative
Citrate	10	2.7	—44.0
Cyanide	20	2.7	—22.4
Cyanide	2	2.7	—7.6
Dichromate	10	2.7	change in hue
Fluoride	1	2.7	—15.4
Fluoride	0.3	2.7	—4.6
Iodide	100	2.7	—30.0
Iodide	50	2.6	variable
Molybdate	10(Mo)	2.5	—27.6
Molybdate	3	2.5	—4.4
Molybdate	1	2.5	negative
Nitrate	200	2.7	negative
Nitrite	10	2.7	change in hue
Phosphate	10 (P_2O_5)	2.7	—30.2
Oxalate	10	2.7	—95.4
Pyrophosphate	1	2.7	—80.0
Silicate	20 (SiO_2)	2.6	slight turbidity
Sulfate	250	2.8	negative
Sulfite	2.5	2.6	—7.4
Tartrate	100	2.9	—53
Thiocyanate	10	2.7	change in hue
Thiosulfate	5	2.7	—11.0
Tungstate	10	2.5	—27.2

Woods and Mellon[18] have studied various methods used for the colorimetric determination of iron, including the use of salicylic acid.

Detection and determination of titanium. Tetravalent titanium in 80-100 per cent sulfuric acid reacts with phenols to give a blood red coloration similar in appearance to that of ferric thiocyanate. A sensitive test for titanium, which is about 5 times as delicate as the well-known hydrogen peroxide test, is obtained with a solution of 10 g. of salicylic acid in 1 liter of concentrated sulfuric acid. The following test is used for the detection of titanium in minerals.[19-22]

Procedure. Fuse the sample with potassium acid sulfate, dissolve the melt in 86 per cent sulfuric acid and add a few crystals of salicylic acid. A red color appears if titanium is present.

By this method 1γ of titanium may be detected in 5 ml. of solution. This reaction cannot be used in the presence of vanadium, molybdenum, and tungsten.

Titanium tetrachloride and salicylic acid in a chloroform solution react to form the compound $Ti(OC_6H_4CO_2H)_2 \cdot TiCl_6$, which is first red in color, and then changes to orange and finally yellow.[23] An orange-yellow precipitate of $HOC_6H_4CO_2TiOOH$ is formed when a solution of sodium salicylate is added to an aqueous solution of the reaction product between titanium chloride and sodium sulfite.[24]

Schenk[20] has used the red color which is formed when a solution of titanium tetrachloride in concentrated sulfuric acid is treated with salicylic acid for the colorimetric determination of titanium. For the determination of titanium, the best conditions are obtained by using an 86-87 per cent solution of sulfuric acid, and 0.2-40 mg. of TiO_2 per liter. Interference with the color developed occurs in the presence of very small quantities of fluorides, iron, molybdenum, columbium, thorium, and zirconium. Tantalum pentoxide does not affect the color. Since interference is caused by substances frequently associated with titanium, the salicylic acid method is of little practical value, but it may be used for a very accurate determination of very nearly pure titanic oxide. Nitrate, nitrite, chromate and permanganate also interfere. The intensity of the color decreases on standing, and this makes impossible the use of permanent color standards. Colorimetric comparison is not used, but the solution may be determined photometrically or by a series of standards method.

Procedure. Fuse 0.5 g. of the sample with 5 g. of potassium carbonate. Dissolve the melt in warm water and add 5 g. of salicylic acid. If any insoluble residue remains, fuse with more potassium carbonate, dissolve, and add to the principal solution. Dilute to 500 ml. If the color is orange instead of yellow, dilute a 100-ml. portion to 1 liter. Compare with a series of standards. These may contain 0.05, 0.1, 0.5, 1.0, 5.0 and 10 mg. TiO_2 per 100 ml. If the color of the more dilute solutions fades, add more salicylic acid.

Mellor[25] has used salicylic acid for the separation of titanium from tantalum and columbium. This separation is based on the following operations: fuse the oxides with sodium bisulfate, dissolve and hydrolyze and treat the extract with ammonium sulfide. Dissolve the precipitate with sulfuric acid and hydrogen peroxide, again hydrolyze, and boil the moist precipitate 3-4 hours with a large excess of salicylic acid. Titanium dioxide dissolves, while the oxides of tantalum and columbium remain insoluble.

Schoeller and Deering [27] have studied this method and report that results obtained by its use are not reliable.

The following procedure is recommended by Muller:

Procedure. Fuse the mixed oxides of titanium, tantalum and columbium with 5 g. of potassium carbonate, leach with water, and boil the liquid with 15 g. of salicylic acid for 3 or 4 hours. Collect the precipitate, wash with a dilute salicylic acid solution, and ignite, and then repeat the above series of operations several times if necessary. A repetition is necessary if the salicylic acid liquid becomes yellow on boiling. The final pentoxide precipitate is fused with sodium acid sulfate, recovered by hydrolysis, ignited and weighed. The combined salicylate filtrates are concentrated and boiled with ammonia and the precipitate is ignited and weighed as TiO_2.

Schoeller and co-workers [30,31] have developed the so-called oxalate-salicylate method, based on the formation of the titanium complex with salicylic acid for the separation of titanium and tantalum and columbium. For details of this procedure, see section on oxalic acid (page 63).

Dittrich and Freund [28,29] have used salicylic acid for the separation of titanium from zirconium and thorium. The following procedure is recommended for the separation of titanium and zirconium:

Procedure. Dissolve 10 g. of ammonium salicylate in 50 ml. of water and heat the solution to boiling. Add dropwise so that the solution does not stop boiling a mixture of titanium and zirconium nitrates which have been neutralized with sodium carbonate. Heat the solution for some time and dilute to 150-200 ml. Filter, as hot as possible, and wash with a boiling hot solution of ammonium salicylate. Ignite to constant weight as ZrO_2. Results obtained with this method are within 1 per cent of the theoretical value.

Thorium and titanium may be separated by a similar procedure.

Detection and determination of copper. Jorissen [63] and Schott [34] have proposed a test for copper which depends upon the red color which is formed when a solution of salicylic acid and potassium nitrite are added to a solution of a copper salt. The following procedure is used:

Procedure. To 10 ml. of the solution to be tested, add 5 drops of a 2 per cent solution of potassium nitrite, 5 drops of a 10 per cent solution of acetic acid, and 3 ml. of a 0.5 per cent solution of salicylic acid in 10 per cent alcohol, and then heat to boiling on a water bath for 45 minutes. A red color appears if copper is present.

Sucrose, glucose, lactose, invert sugar and traces of iron do not interfere with this reaction, but free mineral acids, tartaric acid, citric acid and large quantities of iron mask the color.

The color reaction reported by Jorissen [63] has been used for the colorimetric determination of copper. It has been claimed that the color fades rapidly, but Sherman and Cross [64] state that the color is stable overnight. This is confirmed by Muller and Burtsell.[38]

The following procedure is proposed by Yoe.[35]

Reagent. *Salicylic acid solution:* Use a 0.5 per cent solution in dilute alcohol.

Acetic acid solution: Use a 10 per cent solution of iron-free acetic acid.

Potassium nitrite solution: Dissolve 2 g. of potassium nitrite in 100 ml. of distilled water.

Standard copper solution: Dissolve 0.3928 g. of pure copper sulfate, $CuSO_4 \cdot 5H_2O$, in water, dilute to 1 liter and mix thoroughly. One ml. of this solution contains 0.1 mg. of copper.

Procedure. Dissolve the sample in water and dilute to 10 ml. in an ordinary test tube. Select a number of test tubes to match, as nearly as possible, the sample tube, and to each add a measured quantity of the standard copper solution. The quantities of the standard should vary from 0.1 to 1.0 ml. and each is then diluted to 10 ml. To each tube, including the sample, add 5 drops of potassium nitrite solution, 5 drops of acetic acid solution, and 3 ml. of the salicylic acid solution. Mix thoroughly the contents in each tube, heat to boiling on a water bath for 45 minutes and compare the sample with the standards. This method is sensitive to 0.01 mg. of copper.

The interference is the same as that described above for the qualitative detection of copper.

Shakhkeldian [36] has used salicylic acid in conjunction with benzidine for the colorimetric determination of copper. For this procedure, see section on benzidine. Maier [37] has studied the method of Shakhkeldian and has observed that the color changes quickly in intensity and varies with the age of the sodium salicylate solution and the quantity of the potassium cyanide present. He claims, however, that reliable results may be obtained by careful attention to detail.

Muller and Burtsell [38] have studied many methods for the determination of copper and recommended salicylic acid as one of the most suitable reagents. They state that 4γ of copper per ml. can be determined with an accuracy of 5.3 per cent.

Detection and determination of aluminum. A solution of sodium salicylate gives with aluminum salts a precipitate consisting of fine needles which cluster into spheroids. Cesium chloride facilitates the crystallization. The crystals are soluble in an excess of sodium salicylate. Salts of iron and chromium also give precipitates but they are distinguishable from the aluminum crystals both by color and crystalline form. Small amounts of iron and aluminum may be detected by the brown color of the crystals. Treatment with ammonia aids in the differentiation of iron and chromium.[39]

Aluminum may be determined from neutral solutions of aluminum salts by precipitating as basic aluminum salicylate and igniting to Al_2O_3. The basic aluminum salicylate precipitate can be filtered much more rapidly than the hydrous aluminum oxide, and results obtained by this procedure are more satisfactory than those obtained by the lithium aluminate method. The composition of the aluminum precipitate is somewhat variable.[40]

Pavlinova[41] has used sodium salicylate in a titrimetric procedure for aluminum. When a neutral solution of an aluminum salt is treated with sodium salicylate, an equivalent quantity of free acid is formed. Thus, aluminum may be determined indirectly by titrating the solution with a standard base. The determination is carried out by adding 9-10 moles of sodium salicylate per mole of aluminum, and then titrating with 0.1 N sodium hydroxide solution. The titration is first carried out in the cold, and then is finished after boiling. Phenolphthalein is used as the indicator. The average error using this method is 0.28 per cent.

Detection of silver, lead and mercury. An intense brown color is produced by the addition of as little as 0.01 mg. of silver in an aqueous solution of its salt, to a solution of ammonium salicylate and ammonium persulfate.[42] Silver may be detected by means of this reaction:

Reagent. *Ammonium salicylate solution:* Neutralize 20 g. of salicylic acid with ammonium hydroxide and add a slight excess of the latter. Dilute the solution to 1 liter.

Ammonium persulfate solution: Dissolve 50 g. of ammonium persulfate in water and dilute to 1 liter.

Procedure. Add the solution of the silver salt to a mixture of 20 ml. of the ammonium persulfate solution and 20 ml. of the ammonium salicylate solution. An intense brown color forms if silver is present.

Lead does not give this reaction. As little as 1.1 mg. of silver can be detected in the presence of 0.2 g. of lead.

The brown substance formed in the above reaction does not contain silver, and consequently the latter probably acts as a catalyst in the reaction between the salicylic acid and persulfate. This appears to be true since upon boiling the solution of ammonia salicylate and ammonium persulfate a similar brown color is obtained.

Martini and Baro Graf[43] have used sodium salicylate for the microchemical detection of silver, lead and mercury. Salicylates with solutions of silver compounds give characteristic crystals at concentrations as low as 1 part of silver in 20,000 parts of solution.

Mercuric nitrate also gives characteristic crystals at a dilution of 1:20,000. Mercuric chloride does not give a similar reaction. Lead salts give a test at a concentration of 1:1000.

Determination of uranium. Canneri and Fernandes[44] have studied the various procedures for separating the rare earths from uranium, and report that the procedure of Nilson,[45] which depends upon precipitation with an alkali oxalate, is not satisfactory since some uranium is carried down, and also because the rare earths are not completely precipitated.[46] Since uranium tends to form stable heteropoly compounds with the hydroxy organic acids, these compounds have been used in an attempt to separate uranium from the rare earths. The uranyl tartrates are not suited for this purpose.[47]

Canneri and Fernandes [44] have used salicylic acid for the separation of lanthanum and uranium.

Procedure. Treat the hot weakly acid solution containing lanthanum and uranium with an excess of salicylic acid, and add ammonium hydroxide dropwise until the solution becomes red. Care must be taken that ammonium hydroxide is not added in excess, since the solution must remain acid. If the solution does become alkaline, restore the acidity by the addition of more salicylic acid. Add a small excess of a concentrated solution of ammonium oxalate and boil the solution. Allow the precipitate to settle and filter, and wash the residue with a boiling solution of ammonium oxalate. Determine lanthanum by igniting the oxalate residue and weighing. Acidify the filtrate, which contains the uranium, with concentrated hydrochloric acid and allow to cool, and then filter to remove most of the salicylic acid. Wash the precipitate with cold water and evaporate the combined filtrate and washings to dryness, and ignite on a sand-bath to remove organic matter. Dissolve the residue in hydrochloric acid, boil, filter and precipitate uranium as ammonium pyrouranate by the dropwise addition of ammonium hydroxide.

When a solution of sodium pyrouranate is heated with salicylic acid, sodium uranyl salicylate separates on cooling. This compound has a composition represented by the formula, $[HO{-}C_6H_4{-}CO_2Na]_2UO_2$.

Similar compounds are formed with potassium and ammonium.

The color reaction which is obtained when salicylic acid reacts with uranyl salts has been used by Muller for the colorimetric determination of small quantities of uranium.[48] Uranium should be in the form of uranyl nitrate. Iron and organic solvents, such as alcohol and acetone must be absent.

Procedure. Treat 5 ml. of a 0.2 per cent uranyl salt solution with 5 ml. of a 2 per cent solution of salicylic acid, and compare the resulting red color with that obtained by treating solutions of known uranium content in the same manner. The comparison is made in a colorimeter. This method is accurate to about 7 per cent.

Detection of manganese. When treated with sodium salicylate and ammonia, salts of manganese give long, pale green needles which are arranged in star-shaped clusters. This reaction has been used by Van Zijp [49] for the microdetermination of manganese. If zinc is present, precipitate with sodium salicylate on a microscope slide. Expose to ammonia until the precipitate dissolves and then observe under a microscope. Greenish-brown needles soon appear around the edge of the drop if manganese is present.

Detection of vanadium. Vanadium is detected by means of the amethyst-violet color which forms when an aqueous or alcoholic solution of vanadium chloride is treated with salicylic acid. As little as 0.17 mg. of vanadium chloride per ml. of solution yields a violet color with the reagent, but with 0.08 mg. of vanadium chloride per ml. an orange color is obtained. If salicylic acid is replaced by sodium salicylate, a reddish-brown color is obtained.[50,51]

Detection of cerium. An almost black precipitate is obtained when a solution of tetravalent cerium is treated with ammonium salicylate. This precipitate is insoluble in an acid solution, but turns brownish-gray when treated with ammonium hydroxide. This recation may be used for the detection of cerium, but is not sensitive enough to be used as a spot test. Thorium, titanium, zirconium, praseodymium, columbium and trivalent cerium do not give this test.[52]

Detection of tungsten. Defacqz[53] and Reichard[50] have used salicylic acid for the detection of tungsten. A yellow compound is formed when sodium salicylate is added to a solution of sodium tungstate which is acidified with hydrochloric acid.

Determination of thorium. Kolb and Ahrle[54] have suggested the use of salicylic acid for the separation of thorium from the rare earths, but this reagent does not seem particularly useful.

Fluorescent analysis of iron, nickel and titanium. Goto[55-57] has used salicylic acid for the detection of iron, nickel, and titanium. As little as 2.5γ of ferric iron in an acetate buffered solution destroys the deep violet fluorescence of salicylic acid. An ammoniacal solution of nickel destroys or weakens the fluorescence of salicylic acid, and, while the test is fairly specific, it is not sensitive. Titanium, like iron, destroys the fluorescence of salicylic acid.

Detection of nitrate and nitrite. Nitrites react with salicylic acid in the presence of sulfuric acid to give a yellowish to red color. This reaction has been used by Loof[58] and others[59-61] for the detection of nitrates.

The original procedure by Loof, which is used for the detection of nitrates in water, is carried out as follows:

Procedure. Dissolve 0.5 g. of sodium salicylate in 5 ml. of the water to be tested, add 10 ml. of concentrated sulfuric acid and mix. A yellowish to red color forms if nitrate is present.

Caron and Raquet[61] recommend the following procedure:

Procedure. Evaporate 10 ml. of the water to be tested to dryness with 1 ml. of a 1 per cent aqueous sodium salicylate solution. Mix the residue with 1 ml. of concentrated sulfuric acid, allow to stand for several minutes, and add 10 ml. of water and finally 10 ml. of ammonia. A yellow color is formed if nitrates are present.

The following procedure for nitrate is suggested by Tingle:[60]

Reagent. Dissolve 2 g. of salicylic acid in 30 ml. of concentrated sulfuric acid.

Procedure. Heat a little of the solid to be tested in a test tube with an excess of the reagent, and transfer a drop of the resulting solution to a cold white spot plate. Add 2 or more drops of concentrated potassium hydroxide solution until the reaction is alkaline. A yellow or orange color appears if nitrates are present.

If the material to be analyzed is in the form of a solution, warm 2 or 3 drops of the solution carefully with 2-3 drops of the reagent until fumes of the acid appear, and allow to cool. When cold add a slight excess of potassium hydroxide as above. A distinct yellow color is obtained with only 1 drop of 0.1 per cent potassium nitrate.

The following method for detecting nitrites has been proposed by Desfourneaux:[59]

Procedure. Add a few drops of a 10 per cent potassium iodide solution and a few drops of a starch solution to 10 ml. of the solution suspected of containing nitrite, and carefully float on this solution 5 ml. of a 6 per cent alcoholic solution of salicylic acid. If nitrite is present, a violet-blue zone appears.

Detection of boric acid. Michel[62] has used salicylic acid to improve the sensitivity and specificity of the well-known turmeric test for boric acid.

Determination of hyposulfites. Roth[16] has used salicylic acid as an indicator and catalyst in a titrimetric method for the determination of hyposulfites.

Procedure. To 25 ml. of water in an Erlenmeyer flask add 1-2 ml. of acetic acid and a little sodium bicarbonate to provide an atmosphere of carbon dioxide. Add 10 ml. of 50 per cent sodium acetate solution and about 0.1 g. of salicylic acid. When the salicylic acid has dissolved, add 10 ml. of a ferric alum solution prepared by dissolving 48.22 g. of the solid in a liter of solution, and then a little more sodium bicarbonate. Finally titrate with a solution of $Na_2S_2O_4$ until the solution becomes colorless.

One mole of $Na_2S_2O_4$ is equivalent to 2 atoms of iron; thus, 1 ml. of 0.1 N ferric solution = 8.706 mg. of $Na_2S_2O_4$.

Alkalimetric and iodometric standard. Salicylic acid may be used as a standard for titrating solutions of the alkali hydroxides with phenolphthalein as the indicator. The values obtained by this method are 0.1 per cent lower than those obtained with oxalic or benzoic acid.[32,33]

The standardization of thiosulfate solutions, based on the reaction

$$IO_3^- + 51^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

may be accurately carried out with the use of salicylic acid.[66] Titration of the liberated iodine with the thiosulfate solution must take place promptly, and not after 30 minutes as recommended by Kolthoff, since there is a tendency for iodine to substitute in the salicylic acid molecule and cause high results.

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SULFOSALICYLIC ACID

Synonym: Salicylsulfonic acid; 2-hydroxybenzoic acid-5-sulfonic acid

$C_7H_6O_6S \cdot 2H_2O$ Mol. Wt. 254.21 Beil. Ref. XI, 411 (106).

$$HO_3S—C_6H_3(OH)CO_2H$$

Use: Detection of iron.

Determination of aluminum, beryllium, calcium, chromium, columbium, copper, iron, lead, manganese, nitrate, sodium, tantalum, thallium and titanium.

Sulfosalicylic acid is a white crystalline solid or a white powder. It is colored pink by traces of iron. The compound is obtained as the dihydrate. It melts at 120° C. when anhydrous and at higher temperatures decomposes into phenol and salicylic acid. A value of 108-113° C. for the melting point of the dihydrate has been reported,[45] but this is said to be correct only if measured immediately after drying in a desiccator. Sulfosalicylic acid is soluble in water, alcohol and ether. The reagent should be stored in a well-stoppered bottle and protected from light.

Commercial sulfosalicylic acid is rarely, if ever, obtained completely ash-free. A product obtained by converting the compound to the lead salt, purifying, recrystallizing several times and subsequently decomposing with hydrogen sulfide, has an ash content of 0.05 per cent. The ash consists largely of lead oxide and calcium oxide. Commercial sulfosalicylic acid has a maximum ash content of about 0.1 per cent, and it is recommended to determine the ash content of each sample before use.

Commercial sulfosalicylic acid should be purified according to the following procedure: prepare a saturated solution of the acid in 96 per cent ethyl alcohol at room temperature, and allow the solution to stand for several days. Filter off the precipitate and repeat the operation several times. In this way all but minute traces of inorganic substances are removed.

Preparation: Mix 10 parts of salicylic acid with 50 parts of concentrated sulfuric acid and heat on a boiling water bath. Solution is complete after a few minutes, but after about a half hour the mass crystallizes to a thick paste and the temperature increases to 108-109° C. Remove most of the excess sulfuric acid with suction, and add the residue to about 20 times as much almost saturated salt solution as the weight of the salicylic acid. Sulfosalicylic acid separates almost completely. Purify by recrystallizing from a concentrated solution of salt.[1]

For the preparation of sulfosalicylic acid as an analytical reagent, it is not always necessary to prepare the compound in the solid form. A solution suitable for many analytical procedures is prepared as follows:

Preparation: Treat 50 g. of pure salicylic acid with sufficient concentrated sulfuric acid in a 300-ml. beaker to form a paste. Heat on a sand-bath. With a slight excess of sulfuric acid the entire mass may solidify and in this case heat until the mass is again liquid and the color is changed to a dark orange or a violet-brown. Cool with stirring to prevent the formation of a hard mass. Gradually add water until the mass has dissolved, and add ammonium hydroxide until the violet color changes to yellowish-green. Then add a few drops of dilute sulfuric acid and dilute to 500 ml.

Use double sublimed salicylic acid and purest sulfuric acid to obtain a product free of impurities.

Detection and determination of iron. Ferric iron in an acid solution reacts with sulfosalicylic acid to yield a red color which is similar to that produced with thiocyanates, and the reaction is about equally sensitive.[2] In an alkaline solution sulfosalicylic acid reacts with both ferrous and ferric salts to yield a yellow color.[3] The presence of oxidizing agents causes the yellow color to turn brown. Since the color obtained by sulfosalicylic acid in an acid solution is due only to the presence of ferric iron, and the color in an alkaline solution is due to both ferrous and ferric iron, this reaction may be used for the determination of total iron and both oxidation states.

Contrary to early claims, the depth of color produced with ferric iron in acid solutions appears to be somewhat intensified by the presence of ferrous iron, but a suitable correction for this effect may be applied.[2] The following methods for determining both ferric iron and total iron are taken from the work of Alten, Weiland and Hille:[2]

(a) Determination of ferric iron.

Reagents. *Sulfosalicylic acid:* Dissolve 10 g. of sulfosalicylic acid in 20 ml. of water and add 10 per cent sodium hydroxide until the pH of the solution is 2.0. Finally dilute to 100 ml.

Citrate buffer: Dissolve 21 g. of citric acid in 200 ml. of N sodium hydroxide and dilute to 1 liter. Mix 3 ml. of this solution with 7 ml. of 0.1 N hydrochloric acid. This is the buffer solution.

Procedure. Dilute a solution containing not more than 2 mg. of ferric iron to 20 ml. and add 10 ml. of N ammonium chloride and 1 ml. of a cold saturated solution of α-dinitrophenol. If the solution is alkaline to the indicator, add 0.1 N hydrochloric acid until the yellow color disappears. Carefully add 0.1 N sodium hydroxide solution until a permanent yellow color is obtained, and then add 5 ml. of the reagent solution and 5 ml. of the citrate buffer. Allow the solution to stand for 3-4 hours and compare the resulting color with standards similarly prepared.

(b) Determination of total iron.

Reagents. *Sulfosalicylic acid:* Dissolve 20 g. of sulfosalicylic acid in 100 ml. of water.

Citrate solution: Dissolve 21 g. of citric acid in 200 ml. of N sodium hydroxide and dilute with water to 1 liter.

Borate buffer: Dissolve 12.40 g. of boric acid in 100 ml. of N sodium hydroxide solution and dilute to 1 liter. Mix 46 ml. of this solution with 54 ml. of N sodium hydroxide.

Procedure. To the same quantity of sample as used for the determination of ferric iron, similarly diluted, add 10 ml. of N hydrochloric acid, 2 ml. of reagent solution and 20 ml. of the citrate solution. Now add 10 per cent sodium hydroxide solution until the color is changed from red to yellow, and then add 10 ml. of N sodium hydroxide and 20 ml. of the borate buffer.

Mix well and allow to stand for 4 hours, and compare with standards similarly treated.

(c) Determination of ferrous iron.

The quantity of ferrous iron in the sample is obtained by deducting the quantity of ferric iron from the total iron determined in the above procedures.

Similar methods have been used by Lapin and Kill[4] and by Lorber.[3]

In a recent study of the iron-sulfosalicylic acid reaction, Kennard and Johnson[40] report that the most useful iron concentration ranges from 0.1 to 2.0 mg. of ferric iron per 100 ml. of solution. Measurement at pH 8.2 is the most sensitive, and a pH of 1.5 covers the widest range. They also claim that sulfate should be absent, and that phosphate interferes at pH 5, although a correction may be applied.

Rozanov and coworkers[5,6] report that the method of Alten, Weiland and Hille is not suitable for the colorimetric estimation of ferric iron in the presence of considerable quantities of phosphoric acid ($P_2O_5:Fe_2O_3 = 20:1$). By omitting the addition of the citrate buffer solution and by increasing the quantity of the reagent solution added to five times that recommended originally, it is possible to determine one part of Fe_2O_3 in the presence of one hundred parts of P_2O_5. This modification of the iron procedure makes possible the determination of iron in apatites and phosphorites with results which agree within ±0.23 per cent as compared with values obtained by the Reinhardt-Zimmermann titrimetric method. Aluminum oxide, calcium oxide, silica, chlorides and nitrates do not affect the results but organic substances and ferrous iron are objectionable.

Ferric and ferrous compounds react with sulfosalicylic acid in the presence of ammonium hydroxide to yield a beautiful yellow color. This color varies in intensity with the iron content of the solution, but it is practically unaffected by the concentration of ammonium hydroxide.

Lorber[3] has used this reaction for the microcolorimetric determination of iron in blood.

Reagents. *Sulfosalicylic acid solution:* Dissolve 20 g. of sulfosalicylic acid in 100 ml. of water.

Standard iron solution: Dissolve 0.7032 g. of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ in one liter of water and acidify with 3-4 drops of concentrated sulfuric acid. This solution is equivalent to 0.01 per cent iron.

Procedure. Measure the blood into a Jena test tube with a calibrated 0.1 ml. pipet and oxidize by boiling carefully with 0.25 ml. of a 1:1 sulfuric acid-nitric acid mixture until the mixture becomes entirely colorless. It may be necessary to add a drop of 30 per cent hydrogen peroxide to bring about complete decolorization. Cool, add 3 ml. of water, and boil for 2 minutes. Cool in running water, add 0.4 ml. of the reagent solution and add 10 per cent ammonium hydroxide solution dropwise until the initial red color changes to a bright yellow. Dilute to 5 or 10 ml., depending upon the quantity of iron present, and compare in a colorimeter with a solution containing 0.01 mg. of iron per ml. This is prepared by adding to 10 ml. of the iron standard, 4 ml. of the reagent solution and 4 ml. of ammonium hydroxide, and then diluting the mixture to 100 ml. with distilled water.

When present in large quantity, copper, nickel and cobalt interfere by the formation of a green or brown coloration. The green color due to copper is destroyed by adding a few drops of 5 per cent potassium cyanide solution.

Korenman[7] has used a similar method for the rapid microcolorimetric determination of iron.

Paviot and co-workers[8,9] have used sulfosalicylic acid for the estimation of iron in sputum:

Procedure. Ash the sample and dissolve the ash in 2 ml. of 1:3 hydrochloric acid. Add 2 drops of 30 per cent hydrogen peroxide and 0.5 ml. of a 10 per cent solution of sulfosalicylic acid. Add 1:1 ammonium hydroxide until the pink color changes to yellow. Dilute to 5 ml., and compare the yellow color with that of a standard iron solution which has been similarly treated.

Alimarin and Frid[10] have described the following method for the colorimetric determination of iron in minerals, rocks and ores.

Procedure. Grind the mineral or ore to a fine powder and moisten 10-20 mg. of the sample with 6 ml. of water. Add 3-4 drops of concentrated sulfuric acid and 1 ml. of concentrated hydrofluoric acid, and heat first on a steam bath and finally on a sand bath. Fuse the residue with potassium pyrosulfate, cool, and dissolve the melt in very dilute hot sulfuric acid. Add 1 drop of nitric acid and heat for 1 minute. For each 0.1 mg. of Fe_2O_3 add 3 ml. of 25 per cent sulfosalicylic acid solution, and then add a 25 per cent ammonium hydroxide solution dropwise until the solution turns yellow. Then add 0.5 ml. in excess. Dilute the solution to a definite volume, which is so selected that 1 ml. of the colored solution will contain not more than 0.05 mg. of Fe_2O_3. Allow to stand for 5 minutes, and compare in a colorimeter with a standard solution containing about 0.02 mg. of Fe_2O_3 per ml.

If manganese is present, add 0.2 g. of hydroxylamine hydrochloride before adding the ammonium hydroxide. In analyzing rich manganese ore, add 1.0 g. of hydroxylamine hydrochloride. With samples containing more than 20 per cent aluminum oxide or magnesium oxide, use 5 ml. of the reagent.

Urech [11] has used sulfosalicylic acid for the determination of iron in aluminum and aluminum alloys by employing the principle of colorimetric titration. In this procedure the color produced by sulfosalicylic acid when added to a solution of unknown concentration is compared by adding from a buret a measured volume of a solution of known iron concentration to a vessel containing the diluted reagent.

Thiel and Peter [12] have applied the principle of absolute colorimetry to the method of Lapin and Kill.[4] They claim that from 0.24-8.0 mg. of iron per liter can be determined with remarkable accuracy by this method. In the determination of iron by absolute colorimetry there is no measureable extinction in a solution which contains no iron, so that the use of a compensating solution as recommended by Alten, Weiland and Hille [1] is unnecessary.[13] Thiel and van Hengel [13] have investigated the methods for determining iron with 7-iodo-8-hydroxyquinoline, 2,2′-dipyridyl and sulfosalicylic acid, and have reported that the best results are obtained with the last mentioned reagent. Bencze,[41] on the other hand, favors the use of 1,10-phenanthroline. A number of special methods have been developed for the determination of iron by sulfosalicylic acid in various materials. Among these are: apatites and phosphorites [5,6] and other phosphates;[14] in chrome plating baths;[15] in aluminum and aluminum alloys;[16,17] in aluminum and magnesium alloys;[18] and in boric acid and borax.[19]

Wenger and Duckert [43] recommend a 5 per cent aqueous solution of sulfosalicylic acid as one of the most satisfactory reagents for the detection of ferric iron.

Separation of iron, titanium and aluminum. Trivalent iron and aluminum form complexes with sulfosalicylic acid from which the hydrous oxides cannot easily be precipitated, although ammonium sulfide precipitates iron quantitatively as the sulfide. Tetravalent titanium forms a similar complex with sulfosalicylic acid, but upon boiling the ammoniacal solution, hydrated titanium dioxide is precipitated. Unionized complexes are not formed by sulfosalicylic acid with manganese, calcium, magnesium, and other metals. Consequently sulfosalicylic acid may be used for the separation of iron and aluminum from titanium, manganese, magnesium; and phosphates.[20-22,42] Moser and Iranyi [21,22] recommend the following procedure for separating iron and titanium:

Reagent. Place 50 g. of salicylic acid in a 300-ml. beaker, and add sufficient concentrated sulfuric acid to form a paste. Heat on a sand bath to form the sulfonic acid. With a slight excess of sulfuric acid the mass becomes solid. Heat until the product is liquefied, and the color becomes dark orange or violet-brown. Cool and stir to prevent the formation of a hard mass. Dissolve by the gradual addition of water. Add ammonium hydroxide until the violet color changes to yellowish-green, add a few drops of dilute sulfuric acid, and dilute to 500 ml.

Procedure. Fuse the weighed oxides of iron and titanium with potassium pyrosulfate, and dissolve the melt in cold dilute sulfuric caid. Add 50 ml. of the sulfosalicylic acid reagent, and then add ammonium carbonate until the opaque violet-black solution changes to a clear red. Dilute to a volume of 200 ml. and saturate with hydrogen sulfide. Filter, and during this operation keep the filter filled with the liquid to prevent oxidation of the sulfide. Wash the residue with a solution prepared by mixing 10 ml. of the reagent solution with 200 ml. of water, neutralizing exactly with ammonium carbonate, and saturating with hydrogen sulfide. Next wash with water saturated with hydrogen sulfide until the filtrate no longer gives a violet color when tested with a weakly acid solution of ferric chloride. Ignite and weigh as Fe_2O_3.

To separate titanium and aluminum, precipitate titanium as the hydroxide by ammonium hydroxide in the presence of sulfosalicylic acid. No aluminum is precipitated under such circumstances.[21,22]

Separation of aluminum and iron from manganese. To separate iron and manganese it is necessary only to add sulfosalicylic acid, disodium phosphate, and a little ammonium hydroxide. Under these conditions manganese is precipitated as $MnNH_4PO_4$ while iron remains in solution. Aluminum behaves like iron in this reaction except that a considerable excess of sulfosalicylic acid is necessary to prevent precipitation of aluminum phosphate.

Reagent. Dissolve 33 g. of sulfosalicylic acid in sufficient water to make 100 ml. of solution.

Procedure. To the solution containing ferric and manganese chlorides, add 15-20 g. of solid ammonium chloride and 50 ml. of reagent for each 0.5 g. of Fe_2O_3. Add sodium phosphate, and then ammonium hydroxide dropwise with stirring until the mixture is slightly alkaline. Avoid a larger excess of ammonium hydroxide. Heat the solution almost to boiling, and allow to stand two hours on a water bath until the precipitate changes into gleaming crystals. Filter, and wash with water containing ammonium nitrate until the residue is free of chlorides, and then convert to $Mn_2P_2O_7$ by ignition. The factor for manganese is 0.3870.

Iron is precipitated by treating the filtrate with hydrogen sulfide. The ferrous sulfide is washed with water containing ammonium sulfide until all reagent is removed, and is then dissolved in hydrochloric acid, oxidized with several drops of nitric caid, and iron precipitated with ammonium hydroxide.

Separation of titanium and chromium. Sulfosalicylic acid may also be used to separate titanium from chromium:[23]

Procedure. Fuse the oxides of chromium and titanium with potassium bisulfate and dissolve the melt in cold 6 N sulfuric acid. Add 50 ml. of 15 per cent sulfosalicylic acid solution, and add ammonium hydroxide until the color is grayish-green. Boil, filter, wash, ignite and weigh as TiO_2.

Separation of thallium. Moser and Brukl[24] have used sulfosalicylic acid for the separation of thallium from lead, manganese, aluminum, iron and chromium. To separate thallium from lead proceed as follows:

Procedure. Add a few drops of sulfurous acid, and boil off the excess sulfur dioxide to insure the complete reduction of the thallium to the thallous state. Add 20 ml. of 33 per cent sulfosalicylic acid and an excess of 10 per cent diammonium phosphate solution. Make the solution slightly ammoniacal and allow to stand for several hours. Filter off the precipitated lead phosphate and wash with a very dilute ammoniacal solution containing ammonium nitrate. Lead is determined in the precipitate by igniting and weighing as $Pb_2P_2O_7$. To determne thallium, concentrate the filtrate by evaporation, make slightly ammoniacal, and heat to boiling. Add with stirring, sufficient potassium chromate so that the solution will contain about 2 per cent of this salt. Allow the mixture to stand overnight, wash by decantation with a 1 per cent solution of potassium chromate, and finally wash with 50 per cent alcohol. Dry the precipitate at 120° C. and weigh as $TlCrO_4$. The factor for thallium is 0.7790.

To separate manganese from thallium, precipitate manganese as $MnNH_4PO_4$ and weigh as $Mn_2P_2O_7$. To separate aluminum and thallium, prepare a solution with sulfo-salicylic acid as described above, but determine the thallium first as thallium chromate. Then in the filtrate destroy the organic acid and determine aluminum according to established methods.

Iron and thallium are separated similarly, but for this determination add 10 ml. of reagent for each 0.1 g. of Fe_2O_3 present. Upon boiling this solution the dark violet color of the iron solution turns red but thallium is precipitated as the chromate without contamination. Thallium may be separated from chromium in exactly the same manner as described for thallium and aluminum.

Both thallous and mercuric ions are precipitated by the addition of sodium thiosulfate to ammoniacal solutions of their salts. In the presence of sulfosalicylic acid, however, neither thallium, nor mercury is precipitated with sodium thiosulfate, and only thallium is precipitated by potassium chromate. Thus, sulfosalicylic acid may be used for the separation of thallium and mercury.

Procedure. To the solution containing both thallium and mercury, add 1-2 g. of sulfosalicylic acid for each 0.1 g. of mercury, and then add ammonium hydroxide until the solution is alkaline. If the solution does not remain perfectly clear, an insufficient quantity of sulfosalicylic acid was used. Add 2 g. of sodium thiosulfate, and dissolve any precipitate which forms by heating gently to a temperature not exceeding 35° C. and adding water. Cool, and precipitate thallium by the addition of potassium chromate with stirring.

To determine mercury in the filtrate, add sodium thiosulfate, acidify strongly, and boil. Dissolve the precipitate of mercuric sulfide and sulfur in sodium sulfide, filter, and determine mercury in $Hg(SNa)_2$ by the method of Volhard.

Determination of copper. Tananaev and Litvinenko [25] have used sulfosalicylic acid in a titrimetric procedure for the determination of copper in copper-antimony and copper-aluminum-antimony alloys.

The procedure is based upon the following operations:

Procedure. Dissolve 0.2 g. of the sample and titrate antimony with potassium bromate. Add 15 ml. of 20 per cent sulfosalicylic acid and neutralize with ammonium hydroxide to form the copper-ammonia complex. The resulting solution is clear and has a greenish-blue color. Neutralize the excess ammonia with sulfosalicylic acid and add 5-10 ml. of 20 per cent sulfosalicylic acid in excess. The solution becomes pinkish-yellow in color. Add 2-3 g. of potassium iodide, allow the mass to stand for 5 minutes, and titrate the iodine with standard thiosulfate, using starch as an indicator.

Separation of beryllium from zinc. Beryllium may be separated from zinc by precipitating the latter as zinc sulfide from a dilute sulfosalicylic acid solution in the presence of ammonium acetate.[39]

Separation of iron from aluminum and magnesium. Only magnesium is precipitated by sodium phosphate from a solution containing iron, aluminum and magnesium if an excess of sulfosalicylic acid is present.[44]

Procedure. To each 100 ml. of solution of the three metals, add 50 ml. of 33 per cent sulfosalicylic acid solution for each 0.5 g. of oxide present. Add an excess of ammonium hydroxide and heat to boiling, and then precipitate magnesium by adding all at once sufficient 10 per cent sodium phosphate. Boil several minutes with stirring, and add concentrated ammonium hydroxide until the volume of the solution is one-third larger than the original volume. Cool, and allow to stand several hours, and filter through a filter crucible. Wash the precipitate by decanting with 3 per cent ammonia solution containing 2 ml. of sulfosalicylic acid solution per 100 ml. of solution. Transfer the precipitate to the filter with 2.5 per cent ammonia and wash free of sulfosalicylic acid. This may be determined by a spot test with ferric chloride. Ignite and weigh as $Mg_2P_2O_7$. The factor for magnesium is 0.2184.

Separation of columbium and tantalum. Schwarz [26] has studied the separation of columbium and tantalum according to the method of Powell and Schoeller (page 63), but in which sulfosalicylic acid is substituted for salicylic acid. According to Schwarz the use of sulfosalicylic acid affords an excellent means for the proper adjustment of the acid concentration by making use of the three acid radicals being liberated singly or in combination. Schwarz claimed good results by this method, but Chernikhov and Karsaevska [27] report wide variations in attempts to obtain correct columbium values using this method.

Determination of calcium and oxalic acid. Jendarassik and Takacs[28] have used sulfosalicylic acid in an indirect method for the determination of calcium and oxalic acid. Calcium or the oxalate is precipitated as calcium oxalate, and the washed precipitate is then dissolved in a ferric chloride-hydrochloric acid solution. This solution is treated with sulfosalicylic acid and the intensity of the color formed varies inversely as the concentration of oxalate or calcium.

Reagents. *Sulfosalicylic acid solution:* Dissolve 2 g. of sulfosalicylic acid in 100 ml. of water.

Ferric chloride-hydrochloric acid solution: To 10 ml. of a ferric chloride solution containing 1 per cent of iron, add 10 ml. of concentrated hydrochloric acid and dilute to 500 ml.

Procedure. In a centrifuge tube, graduated at 10 ml., place 2 ml. of a solution containing 5-15 millipercent of calcium, or use a volume equivalent to this amount. Add 5 ml. of 1 per cent sodium chloride solution and 10 drops of 10 per cent ammonuim chloride solution, and then 10 drops of saturated ammonium oxalate solution. Allow the mixture to stand 10-24 hours and separate by centrifuging. Remove the supernatant liquid with a capillary tube and wash four times with 10 ml. of water by centrifuging.

Add 2 ml. of the ferric chloride-hydrochloric acid solution. This step is best carried out by lamp light but if this is not practicable, protect the solution from light by means of black paper. If the solid does not dissolve completely in 2 or 3 minutes rub the crystals with a glass rod. Next add 2 drops of 0.5 N potassium bi-iodate solution and then 1 ml. of a 2 per cent sulfosalicylic acid solution. Dilute to the mark (10 ml.). The color develops immediately. Measure the extinction and determine the calcium content by reference to a standard curve.

Determination of sodium. Muller[29] observed that the sodium salts of various phenolic acids give color reactions with solutions of uranyl salts, and this reaction has been made the basis for a colorimetric modification of the Barber and Kolthoff[30] technique for the determination of sodium.

Darnell and Walker[31] have used the color developed with uranyl zinc sodium acetate and sulfosalicylic acid and sodium acetate for the determination of sodium in biological liquids. The color does not exactly follow Beer's law but it is reproducible and stable to time and temperature.

The method described involves the precipitation of uranyl zinc sodium acetate from an ethyl alcohol solution, the removal of the excess precipitant by washing with ethyl acetate in acetic acid and then with ether, the removal of phosphate as uranyl phosphate, and the photoelectric measurement of the color development by sulfosalicylic acid and sodium acetate.

The following method for determining sodium in blood serum, urine or cerebral spinal fluid is taken directly from the published work of Darnell and Walker: *[31]

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Reagents. *Uranyl zinc acetate reagent:* This reagent is prepared according to the method of Weinbach.[32]

Solution a: Dissolve 77 g. of uranyl acetate, $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$ and 14 ml. of glacial acetic acid by heating and stirring in 400 ml. of water.

Solution b: Dissolve 231 g. of zinc acetate $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ and 7 ml. of glacial acetic acid by heating and stirring in 400 ml. of water.

Mix solutions *a* and *b* while still warm and allow to stand for 24 hours. Filter immediately before using.

Ethyl acetate—acetic acid wash solution: Dilute 300 ml. of C.P. ethyl acetate to 1 liter with glacial acetic acid.

Sulfosalicylic acid reagent: Prepare a 5 per cent sulfosalicylic acid solution and check the concentration by titration against a standard sodium hydroxide solution. Five ml. of the sulfosalicylic acid solution should require 17.25 ml. of 0.100 N. sodium hydroxide for neutralization to a phenolphthalein end-point.

Procedure. For the determination of sodium in blood serum, urine, or cerebrospinal fluid, use 1 ml. of 1 to 10 trichloroacetic acid filtrate of the material, or 0.1 ml. of material wet-ashed by the procedure of Hoffman and Osgood.[33]

In the preparation of trichloroacetic acid filtrates, 1 ml. of biological material is delivered from a pipet (calibrated to deliver the material measured) into 7 ml. of distilled water in a test tube. While shaking the tube gently, 2 ml. of 20 per cent trichloroacetic acid are added. The contents of the tube are thoroughly mixed by stirring and allowed to stand for 10 minutes. After filtration through an ashless filter paper, 1 ml. of the clear filtrate is delivered from a pipet calibrated for delivery of water into a 15-ml. conical centrifuge tube for treatment with uranyl zinc acetate reagent.

In the preparation of ashed samples, 0.1 ml. of the material to be analyzed is delivered from a pipet calibrated to deliver that material into a 15-ml. conical centrifuge tube of heat-resistant glass. After addition of 0.2 ml. of 6 N sulfuric acid and 0.1 ml. of concentrated nitric acid, the tube is placed in a beaker of boiling water for 10 minutes or longer. The tube is then removel from the water-bath and the contents are charred over a free flame. By allowing a small flame from a microburner to strike just above the level of the liquid in the constantly shaken tube, very little danger of loss from spattering is encountered. The tube is allowed to cool while another is being similarly treated. Then one drop of 30 per cent hydrogen peroxide is added from a capillary pipet. The contents are again evaporated over a free flame until sulfur trioxide fumes fill the tube, and are then allowed to cool during the treatment of the second tube. The addition of hydrogen peroxide is continued until, after evaporation to sulfur trioxide fumes, only a colorless drop of liquid remains in the tube. (All tubes in any series are treated with equal amounts of hydrogen peroxide in order to ensure constancy of the blank. Six drops or less will generally be enough to produce a clear solution.) After the final evaporation with hydrogen peroxide, the tube is allowed to cool for 10 minutes or more, and to it is added 0.9 ml. of water. After mixing the contents of the tube, it is ready for treatment with uranyl zinc acetate reagent.

To 1 ml. of solution prepared by one of the methods described above, 5 ml. of freshly filtered uranyl zinc acetate reagent are added. At 5 minute intervals are added seven 0.3 ml. portions of ethyl alcohol. These additions must occupy at least 0.5 hour, and may take longer. After each of the first five additions of alcohol the liquid in the tube is mixed, first by tapping the bottom of the tube to produce a rotatory motion in the upper part of the liquid, then by rolling the tube back and forth between the palms of the hands, thus producing effective mixing in the lowest part of the tube. The last two additions of alcohol serve to wash down the walls of the tube and are allowed to remain layered on the solution. After the last addition of alcohol, the tube is centrifuged at 2000 r.p.m. for 10 minutes, decanted, inverted, and allowed to drain for 5 minutes.

The mouth of the tube is wiped dry and the precipitate is agitated by blowing on it a fine stream of about 2 ml. of ethyl acetate-acetic acid wash liquid. (In the case of urines which contain much phosphate the precipitate must be agitated by stirring with a glass rod, which is washed off with the wash liquid after each use.) The walls of the tube are washed down with a small amount of the liquid. Centrifuging for 10 minutes, draining for 5 minutes, and wiping are carried out as before, and about 5 ml. of ether are used to wash the precipitate and the walls of the tubes. Precipitates from urines must be stirred with a glass rod. The tube is centrifuged for 5 minutes, decanted, and drained for 1 minute. (Longer draining may allow the flaky precipitate to become so dry that it crumbles and falls out of the tube.) The precipitate is washed a second time with 5 ml. of ether, centrifuged 5 minutes, decanted, and drained for 1 minute. The tube is put in a warm place for 5 minutes to evaporate the last traces of ether. To this point the procedure is identical for blood, urine, and cerebrospinal fluid, with the exception of the agitation of precipitates, as noted.

For blood and cerebrospinal fluid, the remainder of the procedure is as follows: The washed, dried precipitate is dissolved in 4 to 5 ml. of water and transferred quantitatively to a 100-ml. volumetric flask. The solution in the flask is diluted to about 70 ml., and to it are added in order 4 ml. of 5 per cent sulfosalicylic acid, 4 ml. of 10 per cent sodium acetate trihydrate, and water to make 100 ml. The contents of the flask are mixed thoroughly and a 15-ml. portion is transferred to an Evelyn colorimeter tube and read in the colorimeter, using the 440 mμ filter. The instrument is set to read 100 with a tube containing 4 ml. each of 5 per cent sulfosalicylic acid and 10 per cent sodium acetate in 100 ml. The optical density, L, is calculated from the formula $L = 2 - \log G$, where G is the corrected galvanometer reading. The concentration of sodium in the sample tube is read from a plot of experimental data or is obtained by dividing L by the correct value of K from the equation $K = 0.889 - 0.1449L$. The sodium content of a similarly treated reagent blank must be subtracted.

If c is the concentration of sodium in the sample tube, b is the concentration in the reagent blank, and v is the volume of biological material taken for analysis, then $100(c-b)/v$ = mg. of sodium per 100 ml. of biological material.

The triple salt precipitated from urine is dissolved by shaking it with 10.00 ml. of water. Any uranyl phosphate present remains in the form of a gelatinous precipitate. The tube is centrifuged for 10 minutes at 2000 r.p.m. Five milliliters of the clear supernatant fluid are pipetted into a 50-ml. volumetric flask, diluted to 35 ml. with water, treated with half-quantities of the color reagents, diluted to volume, and read in the Evelyn colorimeter. The result is calculated in the same manner as in the procedure for blood or spinal fluid, using the above equation.

The recovery of sodium from blood serum and aqueous solution indicates a maximum error of less than 1 per cent for this procedure.

Parks and co-workers[34] have also used the method of Darnell and Walker[31] for the determination of sodium in plant tissue.

Determination of nitrates. Caron and Raquet[35] have suggested the substitution of sulfosalicylic acid for phenoldisulfonic acid for the colorimetric determination of nitrates in water. In the following procedure, the preparation of a special reagent is avoided by using the more generally available salicylic acid:

Procedure. Evaporate a known volume of the sample (10 ml.) with 1 ml. of 1 per cent sodium salicylate solution and to the residue add 1 ml. of pure sulfuric acid. Mix thoroughly, allow to stand for a few minutes, and add 10 ml. of water and finally 10 ml. of ammonium hydroxide. Compare the resulting color with that of standards similarly prepared.

Vasil'eva[36] has used sulfosalicylic acid in place of phenoldisulfonic acid for the determination of nitric acid in chromic anhydride.

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TANNIN

Synonym: Tannic acid, gallotannic acid

Use: Detection of ammonia, barium, calcium, carbon monoxide, cerium, columbium, europium, gadolinium, gallium, gold, iron, lanthanum, lead, mercury, molybdenum, neodymium, phosphorus, praseodymium, samarium, silver, strontium, sulfite, tantalum, thallium, titanium, tungsten, uranium, vanadium and yttrium.

Determination of aluminum, ammonium, barium, beryllium, calcium, carbon monoxide, columbium, copper, gallium, germanium, molybdenum, silver, strontium, tantalum, thorium, titanium, tungsten, uranium, vanadium and zirconium.

Tannin, which is often incorrectly called digallic acid, is a pentadigalloyl esterlike derivative of glucose, and has been assigned the formula $C_{76}H_{52}O_{46}$. The tannin of commerce usually contains about 10 per cent water. It occurs in the bark and fruit of many plants, particularly in the bark of the oak species, in sumac and nyrobalan. It is produced from the Turkish or Chinese nutgall, the former containing about 50-60 per cent of the compound and the latter about 70 per cent. Tannin consists of a yellowish-white to light brown amorphous, bulky powder or flakes. It possesses a faint characteristic odor and an astringent taste. It gradually darkens on exposure to air and light. When heated to 210-215° C. it decomposes largely into pyrogallol and carbon dioxide. The compound yields insoluble precipitates with albumin, starch, gelatin, and most alkaloid and metallic salts. One g. of the solid dissolves in 0.35 ml. of water, and one ml. of warm glycerol. It is very soluble in alcohol and acetone, but is practically insoluble in benzene, chloroform, ether and carbon tetrachloride.

Purity of tannin. Commercial samples of tannin are frequently impure, and are not suitable as analytical reagents. To insure accuracy in quantitative separations, it is essential that the reagent be subjected to purity tests, especially for metals, sugar and dextrin. These tests are carried out as follows:

(1) *Inorganic impurities:* Place 4 g. of tannin in a crucible and ignite. The residue should not weigh more than 5 mg. Dissolve the residue in 2 ml. of acetic acid, dilute with 8 ml. of water and filter through a quantitative filter. To the filtrate add a saturated aqueous solution of hydrogen sulfide. If more than a slight opalescence appears, the sample is unsuited for analytical use.

(2) *Sugar and dextrin:* Mix 10 ml. of a 1:5 solution of tannin in water with 10 ml. of ethyl alcohol (85 per cent by weight). The mixture should remain perfectly clear for one hour. Now add 5 ml. of ether. No turbidity should appear.

(3) *Water content:* When tannin is dried to constant weight at 100° C., the loss in weight should not exceed 12 per cent.

Analytical reactions of tannin. Tannin reacts with a number of cations and anions to form products which are useful in quantitative and qualitative analysis. The reagent is excellent for the detection of titanium, iron, columbium, tantalum, silver, gold, uranium, mercury, vanadates, molybdates, tungstates and phosphates. In quantitative analysis tannin is extremely useful for the separation and determination of many metals, including columbium, tantalum, titanium, aluminum, beryllium, uranium, molybdenum, tungsten, gallium, and germanium. Many other metals such as zirconium, lead, bismuth, antimony and tin are partially precipitated as white solids which are readily soluble in dilute acids. Other metals, such as copper, magnesium, the alkaline earths, manganese, cadmium, zinc, cobalt, nickel, platinum, cerium, thorium and the rare earths either give no reaction with tannin or react only upon the addition of an alkali.

The use of tannin in analytical chemistry is based on the fact that a solution of common tannin or gallotannic acid is essentially a colloidal suspension of negatively charged particles, which are capable of flocculating the positively charged particles of certain inorganic compounds such as the hydrous oxide sols.[104]

Schoeller and co-workers in a series of investigations on the analysis of columbium and tantalum and their mineral associates, have found that certain metals may be classified into groups depending upon their precipitation behavior with tannin. In one group (Group A) are included tantalum, columbium, and titanium, which are precipitated by tannin from a feebly acid oxalate solution which is half saturated with ammonium chloride. The metals of the second group (Group B), which includes uranium, zirconium, thorium, hafnium, aluminum, chromium, gallium and iron, are precipitated by tannin in a neutral tartrate solution containing an alkali acetate. Manganese, beryllium and the rare earths, which belong to the third group (Group C), are precipitated by tannin from an ammoniacal tartrate solution.

Qualitative reactions with tannin. A number of common ions give reactions with tannin which may be used as qualitative tests. Miller [1] has studied the reactions obtained by making the solution of the ion barely acid with acetic or nitric acid, warming, and adding a freshly prepared 10 per cent aqueous solution of tannin. These results are summarized below. The reactions described are for solutions of pure ions, but since many ions give somewhat similar reactions, tannin is not always a useful qualitative reagent.

(a) *Titanium:* Tannin reacts with trivalent titanium to yield a brick-red precipitate or a bright red color, and with tetravalent titanium to give an intense vivid red color. By reating titanium compounds with tannin and 30 per cent hydrogen peroxide, the sensitivity of the reaction is increased, and easily serves to detect 0.05 mg. of titanium in 100 ml. of solution.

(b) *Columbium:* When tannin is added to a boiling solution of columbium in an oxalic acid-ammonium oxalate solution, a bright red complex is formed. This reaction is sensitive to 1 mg. of columbium in 100 ml. of solution.

(c) *Tantalum:* A straw-colored yellow precipitate is formed when tannin is added to tantalum which is dissolved in an oxalic acid-ammonium oxalate solution. This reaction is sensitive to 1 mg. of tantalum in 100 ml. of solution, and constitutes one of the very few satisfactory tests for tantalic salts. When the tannin test is applied to a mixture of the tantalic and columbic oxyacids, the precipitate ranges in color from yellow to red, and this may be used as an index of the composition of the mixture.

(d) *Iron:* Ferric salts react with tannin to give a blue-black color or a black finely divided precipitate. This reaction is sensitive to 0.1 mg. of iron in 100 ml. of solution.

(e) *Silver:* Very dilute solutions of silver salts, which are made slightly alkaline by the addition of an excess of ammonia, are rapidly reduced by tannin to form solutions which appear olive-green in reflected light and reddish-brown in transmitted light. The sensitivity of this reaction, when applied to a boiling solution, is 0.1 mg. of silver per 100 ml. of solution.

(f) *Gold:* Solutions of gold chloride which have been made neutral by the addition of potassium carbonate are reduced to a cherry-red colloidal gold suspension when treated with tannin and heated below the boiling point. The sensitivity of this reaction is 0.1 mg. of gold per 100 ml. of solution.

(g) *Uranium:* Quantities of uranium salts ranging as low as 1 mg. per 100 ml. of solution give an intense brownish color with tannin.

(h) *Mercury:* Tannin yields a yellowish-white precipitate when added to solutions of mercuric nitrate. In the presence of 2 ml. of nitric acid, this reaction can be used to detect 1 mg. of mercury in 100 ml. of solution.[89]

(i) *Vanadates:* One of the most delicate of the tests which have been proposed for vanadium compounds consists of the intense blue-black color or black precipitate which forms when tannin is added to solutions of metavanadates. Vanadates in concentrations as low as 0.05 mg. per 100 ml. of solution are detected by means of the blue color.[57-59,91]

(j) *Tungstates:* Tungstates react with tannin to yield a bright orange color. This reaction is sensitive to 1 mg. of tungsten per 100 ml. of solution, but cannot be used in the presence of molybdates.

(k) *Molybdates:* Molybdates in dilute acetic acid or neutral solutions react with tannin to yield a distinctive brown color or brownish precipitate. This reaction may be used to detect molybdenum in concentrations as low as 0.1 mg. of molybdenum in 100 ml. of solution.

(l) *Phosphates:* Phosphates react with tannin to yield a heavy white precipitate, but the reaction is not very sensitive. Microscopically, however, the test is very distinctive.

Determination of tantalum and columbium. In an important series of investigations, Schoeller and co-workers exhaustively studied the analytical reactions of tantalum and columbium and their mineral associates, and in a number of important papers, the first appearing in 1925, these investigators published a satisfactory procedure for the complete analysis of tantalum and columbium minerals. This series of papers concludes with a summary and index of all the preceding publications.[2]

One of the accepted methods of recovering columbium and tantalum in mineral analysis consists of fusing the material to be analyzed with potassium bisulfate and dissolving the melt in a tartaric acid solution. The tartaric acid solution of the "earth acids" (Ta_2O_5 and Cb_2O_5) undergoes a hydrolytic precipitation when boiled with an excess of nitric or hydrochloric acid. This is referred to as *tartaric hydrolysis.* The precipitate obtained by this treatment is purer than that formed in the usual pyrosulfate hydrolysis. The precipitation of tantalic and columbic acids, and also tungstic acid, is never quite quantitative, since a few milligrams of these substances always remain in solution. Schoeller [3,4] proposes for the separation of tantalic and columbic acids, a tartaric hydrolysis supplemented by tannin precipitation. This is suggested because the tartaric hydrolysis reaction is more specific than tannin precipitation, and permits a more selective precipitation to yield a principal earth acid fraction. This also contains all tungstic acid and small quantities of other oxides, if any are present as impurities. The tannin precipitation is important because it makes possible the recovery of the last traces of the earth acids, together with other oxides which may be quantitatively precipitated. Studies of tannin precipitation reveal that the precipitation of the earth acids is somewhat indefinite with respect to the more important constituents of earth acid minerals, and the analysis of these minerals therefore is based upon a process of fractional separation which eventually leads to the final precipitation of the pure oxides. This fact, combined with the fact that the tannin precipitates are very voluminous, constitutes a serious disadvantage in the use of tannin. Nevertheless, tannin has become an indispensable reagent in earth acid analysis, since no other has been discovered which is capable of giving comparable results.

The following procedure, described by Schoeller, and which is a modification of a method originally proposed by Schoeller and Webb,[3] may be used for the recovery of the oxides of tantalum and columbium from the tartrate solution:

Procedure. To the boiling acid tartrate solution of the bisulfate melt of the mineral, which should have a volume of 200 ml., add 25-30 ml. of concentrated hydrochloric acid and continue to boil for 10 minutes. Collect the precipitate which is formed, wash, ignite and weigh as Ta_2O_5 and Cb_2O_5. Combine the filtrate and the washings and nearly neutralize with silica-free ammonium hydroxide. Evaporate to a volume of less than 150 ml. and treat with ammonia, ammonium sulfide and 5 g. of ammonium acetate. Filter off any iron sulfide which precipitates. Make the filtrate, which should have a volume of 200 ml., slightly acid with acetic acid, remove the hydrogen sulfide by boiling, and treat the boiling solution with a freshly prepared solution containing 1 g. of tannin. The precipitate which forms is free from iron and silica. Wash the precipitate and ignite to Ta_2O_5 and Cb_2O_5. The total weight of the earth acids present is equal to the sum of the weights of the two precipitates obtained in this procedure.

The addition of columbium to stainless steel to improve its corrosion resistance has created a demand for an accurate method for the separation and determination of this element. In the presence of titanium, satisfactory results are obtained by an application of the tannin method, but in most commercial steels containing columbium the quantity of titanium is small enough to make this procedure unnecessary. Cunningham[5] has determined the tantalum content of the total oxides of columbium and tantalum of a columbium-bearing 18 per cent chromium-8 per cent nickel steel by modification of Schoeller and Powell's procedure.[6]

The following description is taken directly from the published method by Cunningham:

Procedure. For this separation the precipitate is fused with 12 times its weight of potassium pyrosulfate and the melt, when cool, is dissolved in 100 ml. of hot 2 per cent ammonium oxalate. The solution is treated with 2 ml. of sulfuric acid 1:1, diluted to 250 ml. with hot water, and heated to boiling. Four drops of a 0.25 per cent solution of bromophenol blue (prepared by dissolving 0.25 gram of the indicator in 7.5 ml. of 0.05 N sodium hydroxide and diluting with cold water to 100 ml.) are added, followed by ammonia

(1:2) drop by drop until the yellow color just changes to a distinct purple. This corresponds to a pH of approximately 4.6. From 25 to 30 ml. of a freshly prepared 1 per cent solution of tannin are added, followed by 10 g. of ammonium chloride and some ashless paper pulp, and the solution is gently boiled for at least 15 minutes.

The hot solution is filtered on an 11-cm. paper containing some ashless paper pulp, and the paper and precipitate are washed from 20 to 25 times with a hot 2 per cent solution of ammonium chloride and ignited in platinum at a low temperature to burn off the carbon of the filter paper. The precipitate is treated in platinum with 5 ml. of sulfuric acid (1:1) and 1 ml. of hydrofluoric acid, and the solution is evaporated to a volume of 1.5 to 2 ml., cooled, and transferred to a 250-ml. beaker by means of 150 ml. of cold 2 per cent hydrochloric acid. Twenty-five milliliters of sulfurous acid and some ashless paper pulp are introduced, the solution is boiled for at least 5 minutes, and allowed to stand for 30 minutes or longer at about 70° C. before filtering. The precipitate is ignited and weighed. A weight of 0.0200 gram of pure titanium dioxide is added, the mixture is fused with 12 times its weight of potassium pyrosulfate and the melt is dissolved as described above. The solution is passed through a reductor and titrated with standard 0.05 N potassium permanganate. A blank on the reductor and titanium dioxide is carried through as described and the difference in volume of permanganate between the sample and the blank is the volume equivalent to any Cb_2O_5. The weight of $Ta_2O_5(+Cb_2O_5)$ less the Cb_2O_5 found, multiplied by 81.91 and divided by the weight of sample taken, gives the percentage of tantalum.

Separations with tannin. The order in which metals are precipitated by tannin from oxalic acid solutions is given in the following series:

Tantalum
Titanium
Columbium
Vanadium
Iron
Zirconium
Hafnium
Thorium
Uranium
Aluminum

The position which chromium occupies in this series has not been determined. The order in which metals are precipitated quantitatively from chloride solutions is given as [96]

Tin
Zirconium
Titanium
Thorium
Vanadium
Molybdenum (III)

In applying tannin to the separation of metals in this series, it appears impossible to separate two adjacent members except by an elaborate system of repeated crystallizations. With metals lying farther apart, however, many useful separations can be made.

Separation of tantalum and columbium. Tantalum and columbium may be separated by taking advantage of the difference in the extent to which oxalotantalic and oxalocolumbic acids are affected by hydrolysis. Oxalotantalic acid is stable only in the presence of oxalic acid but oxalocolumbic acid is relatively much more stable. Tannin favors the hydrolysis of the tantalum compound, and the precipitate formed on boiling the slightly acid solution is probably an adsorption product of tannin and tantalic acid. The method, while practicable, does not afford a clear-cut separation in a single precipitation. The method is subject to error due to the contamination of the precipitate by adsorption, and the danger of incipient precipitation of columbium because of the very narrow range which exists between the complete precipitation of tantalum and the partial precipitation of columbium.[7] Tantalum and columbium are quantitatively precipitated by an excess of tannin from an oxalate solution upon neutralizing by the addition of ammonia. By the carefully regulated addition of the reagents, however, it is possible to effect a separation of these two elements. Tantalum is precipitated from a slightly acid solution as a yellow complex, and columbium is precipitated as a red complex. There is danger of co-precipitation of the columbium complex with tantalum, but this is easily detected by the orange color of the tannin precipitate. Since it is impossible to precipitate tantalum quantitatively without contamination by columbium if the tantalum concentration is lower than that of columbium, it is necessary to separate these two elements by a process of fractional precipitation. The standard procedure calls for the formation of three fractions:[8]

(a) A yellow columbium-free precipitate of the tantalum complex; (b) an orange to red precipitate which consists of both the columbium and tantalum complexes; and (c) a tantalum-free filtrate which contains columbium. The quantitative separation is achieved by a systematic retreatment of the mixed fraction. This is fractionated as before yielding an additional three fractions and the mixed fraction may, if necessary, be again fractionated. The pure columbium is obtained by combining the pure filtrates, and the tantalum is recovered by combining all the yellow, pure tantalum precipitates.

Wirtz[9] has studied the effect of pH upon the precipitation of tantalum and columbium with tannin, and has found that tantalum does not precipitate until a pH of 2.4 is attained, but that columbium precipitates appreciably at pH of 1.9. This range makes possible a satisfactory separation of tantalum and columbium. Very little columbium is precipitated with tantalum at the proper pH range. Wirtz[10] has found that in the presence of bromophenol blue indicator all the tantalum and very little columbium can be precipitated by means of tannin. The small quantity of columbium which is contained in the tannin precipitate is determined by dissolving the oxide which is formed on ignition, reducing, and titrating with potassium permanganate solution. Bleyenheuft[11] has studied the separation of tantalum and columbium by means of tannin and reports that with proper care the method is very accurate.

Powell and Schoeller[7] describe the following method for the separation of tantalum and columbium:

Procedure. Fuse 0.25-0.50 g. of the oxide mixture with 3-6 g. of anhydrous potassium pyrosulfate in a quartz crucible. The greater the quantity of columbium present, the larger the sample used. Not more than 0.25 g. of tantalum oxide must be present because of the voluminous character of the tannin precipitate. If the product of the fusion is not clear, add 0.5-1.0 ml. of sulfuric acid and repeat the fusion.

Cool the melt, and boil with a saturated solution of 2-4 g. of ammonium oxalate. Break up any lumps with a glass rod. If columbic and tantalic acids pass into solution slowly, add several drops of dilute sulfuric acid.

If a clear solution is not obtained, filter any residue and collect the filtrate in a 500-ml. beaker. Wash the residue with hot water. Ignite the paper and residue, and again fuse with potassium pyrosulfate. Dissolve the melt in ammonium oxalate solution as before, and add to the main solution. Filter to remove any insoluble material, such as silicic acid and calcium oxalate.

The solution now contains all tantalum and columbium as the oxalic acid complexes, and also a small quantity of free oxalic acid. The volume of the solution should be adjusted so that there is 0.1 g. of tantalic and columbic acids in 100-150 ml. Heat to boiling and add 10 ml. of a freshly prepared 2 per cent tannin solution. If a permanent turbidity does not appear on boiling, add from a buret a 0.5 N solution of ammonium hydroxide until a permanent turbidity is formed.

From the color of the precipitate, an approximate ratio of the quantities of the two metals may be estimated: if the color is orange to red, columbium is present in excess; but if the color is sulfur-yellow, the mixture contains at least one-third tantalum oxide. The amount of tannin still to be added is determined from the color of the precipitate. For small quantities of tantalum oxide, approximately a 10-fold excess of tannin is used; but at least 0.2 g. of tannin is always used. For larger quantities of tantalum, the quantity of tannin required is obtained from Table 14.

TABLE 14.

Ta_2O_5 g.	Tannin Required g.
0.03	0.2
0.03-0.06	0.3-0.4
0.06-0.12	0.5-0.6
0.12-0.18	0.7-0.8
0.18-0.25	0.9-1.0

Now add 5 g. of ammonium chloride in the form of a saturated solution to the boiling mixture, and boil for 10-15 minutes after precipitation begins. If the precipitate (P_1) is orange to red in color, proceed according to Method A, if sulfur-yellow, use Method B.

Method A: The precipitate should be completely coagulated and settled, and the supernatant liquid should be free of color or turbidity. A straw-yellow color is not significant. If the mixture does not have these characteristics, continue boiling and add 0.5 N ammonium hydroxide until it does.

Filter the precipitate on a black band filter and wash with a 2 per cent ammonium chloride solution. Heat the filtrate to boiling and add 5-10 ml. of the tannin solution. Add 0.5 N ammonium hydroxide until the orange to red color is discharged and a precipitate is formed. Heat the mixture for some time on a water bath and allow to stand overnight. Filter this precipitate (P_2) and wash with 2 per cent ammonium chloride solution. Combine precipitates P_1 and P_2 and ignite in a quartz crucible. Weigh the ignited oxide mixture. Fuse the oxides and treat exactly as described in the first part of this procedure, except instead of using Method A, use Method B, which is described below.

Method B: Allow the mixture to stand until the precipitate has settled and filter through a black band filter. Wash with a 2 per cent ammonium chloride solution. Transfer the precipitate from the beaker to the filter, and add the filtrate to the same beaker. Evaporate to about three-fourths its original volume, and add the wash solution previously separated together with several ml. of tannin solution to the boiling solution. Slowly add from a buret a 0.5 N ammonium hydroxide solution until the orange-red color disappears. Now add 10-25 ml. portions of saturated ammonium oxalate solution until the yellow precipitate begins to coagulate and the supernatant liquid remains clear and colorless. Keep on a water bath for some time and then allow to stand overnight. Filter the precipitate and treat as described in Method A. Combine both precipitates, ignite in a quartz crucible, and weigh as Ta_2O_5.

The filtrate from the second precipitation should be tested for completeness of precipitation by treating with ammonium hydroxide and ammonium oxalate as described above. If a small quantity of tantalum is present, filter off the yellow precipitate, ignite in a quartz crucible, and add the weight to that of the main ignition product.

Separation of columbium and tantalum from titanium. One of the more important separations required in the analysis of tantalum and columbium minerals is that of titanium from tantalum and columbium. This problem was originally studied by Schoeller[12,13] and later by Schoeller and Jahn.[14] They recommend the use of the so-called *oxalate-salicylate* method. This consists of precipitating the earth acids with calcium chloride from an oxalate solution containing sodium salicylate. The oxalic acid in the precipitate is destroyed with potassium permanganate in a hydrochloric acid solution and the earth acids are then precipitated with tannin. The precipitate contains the greater portion of the earth acids. The yellow salicylate filtrate which is obtained from this precipitation is then precipitated with tannin and ammonium acetate.[8] The ignited precipitate is largely titanium dioxide, but in addition it contains a small quantity of the earth acids. These are recovered by a bisulfate fusion and extraction of the melt with an acid solution of tannin. With this treatment the titanium passes into solution while the earth acids remain in the residue. The total earth acids are found by adding this small residue to the principal fraction obtained by the original precipitation. Results obtained using this method are shown in Table 15.

TABLE 15.—SEPARATION OF COLUMBIUM AND TANTALUM FROM TITANIUM

M_2O_5* Used g.	M_2O_5* Found g.	Error g.	TiO_2 Used g.	TiO_2 Found g.
0.2023	0.2015	—0.0008	0.0516	0.0508
0.2027	0.2003	—0.0024	0.0513	0.0512
0.1965	0.1943	—0.0022	0.0535	0.0531
0.0335	0.0339	+0.0004	0.2010	0.1985
0.0439	0.0439	0.0000	0.2067	0.2068
0.1257	0.1258	+0.0001	0.1176	0.1173

* $M_2O_5 = Cb_2O_5$ and Ta_2O_5.

Bykova [16-18] has used the following method for the separation of columbium from titanium in the analysis of titano-columbite:

Reagent A. Dissolve 1 g. of tannin in 5 ml. of hydrochloric acid (*d* = 1.19) and 95 ml. of water.

Reagent B. Dissolve 1 g. of tannin in 10 ml. of hydrochloric acid (*d* = 1.19) and 90 ml. of water.

Procedure. Dissolve 0.2-0.3 g. of the mixed oxides in 2-3 ml. of hydrofluoric acid in a platinum crucible by heating on a water bath. Heat to remove as much of the hydrofluoric acid as possible, and to the syrupy residue add a solution of 1 g. of tannin and 5 ml. of concentrated hydrochloric acid in 95 ml. of water (Reagent A). Mix well, transfer to a beaker, and dilute to 200 ml. Mix and add 8 g. of boric acid. Boil for 5-10 minutes and allow to cool. When cold allow to stand for several hours. Filter and wash with a solution prepared by diluting the precipitant with an equal volume of water. Wash the precipitate back into the original beaker with 100-200 ml. of Reagent B.

Boil the mixture for 15 minutes, cool, and filter through the same filter. Wash with Reagent B that has been diluted with an equal volume of water and then ignite and weigh.

Repeat the above operation two times using only Reagent B. The final fraction of the earth acids is free of impurities except for traces of TiO_2, which amounts to less than 1 mg.

Combine all the filtrates from the separation and neutralize with ammonium hydroxide. Neutralize the excess ammonia with acetic acid, add 10-15 g. of ammonium acetate, 1-2 g. of tannin dissolved in water, and heat to boiling. Cool, filter, wash with 2 per cent ammonium acetate containing a small quantity of tannin, and transfer back to the beaker in which the precipitation was carried out. Treat with 50 ml. of Reagent B diluted with an equal volume of water, and boil for 20-30 minutes. Cool, filter, and again treat the precipitate with Reagent B diluted with water. Ignite and treat the ignited precipitate with hydrogen fluoride and sulfuric acid and again separate the earth acids with Reagent B. Combine the separated earth acids with the principal fraction obtained in the first precipitation and then determine colorimetrically the traces of titanium oxide which remain.

Separation of columbium and tantalum from zirconium. Tantalum and columbium may be separated from zirconium by making use of the fact that tantalum and columbium are completely precipitated by tannin from a barely acid oxalate solution which is half saturated with ammonium chloride, while zirconium (and hafnium, thorium and other metals) are not precipitated under these conditions. A complete separation is possible using this procedure.[19,20]

Like titanium, zirconium is also separated from tantalum and columbium by fusing the mixed oxides with potassium bisulfate, and extracting the fusion product with 5 per cent sulfuric acid containing 1 per cent of tannin. The earth acids remain insoluble as colored tannin-complexes while the sulfates of titanium and zirconium pass into solution.[13]

Separation of columbium and tantalum from uranium. Uranium, like zirconium, thorium, aluminum and iron, may be separated from tantalum, columbium and titanium by adding tannin to a faintly acid oxalate solution which is half saturated with ammonium chloride. Uranium is not precipitated under these conditions.[36]

Separation of columbium and tantalum from rare earths. In a study of the reactions of tannin with the rare earths, Schoeller and Waterhouse[21] found that tannin complexes of these metals are precipitated by the addition of tannin and an excess of ammonium hydroxide. Precipitation also takes place in tartrate solutions. The precipitates are colorless, although an excess of the reagent causes a pale brown discoloration. The complexes dissolve readily in acetic acid. The following procedure is recommended for the separation of the rare earths from the earth acids: precipitate the greater part of the earth acids by tartaric hydrolysis and recover the rare earths and the remainder of the earth acids by tannin precipitation from the ammoniacal filtrate. Fuse the ignited tannin precipitate with potassium bisulfate, extract the melt with an oxalic acid solution or dissolve the melt in tartaric acid solution, and precipitate the rare earths from an oxalic acid solution.

Separation of columbium and tantalum from vanadium. Schoeller and Webb[22] studied the effect of the presence of phosphates and vanadium upon the determination of tantalum and columbium. Some phosphate, if present, precipitates with tantalum and columbium. Vanadium gives a blue-black precipitate with tannin, and a mere trace of vanadate is recognized in this way. In an oxalate solution which is half saturated with ammonium chloride, tantalum, columbium and titanium are precipitated completely with tannin, while zirconium, thorium, aluminum, uranium and beryllium remain in solution. A similar procedure may also be used to separate vanadium from titanium and tantalum, but not from columbium. In separating tantalum and titanium with tannin, it is necessary to omit the neutralization with ammonium hydroxide, which leaves the solution sufficiently acid to prevent complete precipitation of columbium. By combining tartaric hydrolysis, tannin precipitation and the pyrosulfate-tannin procedure, it is possible to obtain a good separation of vanadium and columbium. The ranges of acidity at which columbium and vanadium precipitate with tannin overlap, and so it is impossible to separate vanadium and columbium with tannin alone.

Separation of columbium and tantalum from other metals. When columbium and tantalum are precipitated by tartaric hydrolysis an incomplete precipitation of tungsten may occur. Tannin does not precipitate tungsten alone from tartrate or oxalate solutions, but when enough tantalum or columbium is present, some tungsten is precipitated. For this reason tungsten may interfere in the determination of tantalum and columbium.[23] Antimony, bismuth and copper also interfere, but these metals may be removed satisfactorily by precipitation with hydrogen sulfide. Tantalum and columbium are then determined with tannin.[24]

Schoeller and Webb [25] studied the determination of tantalum and columbium in the presence of tin, and recommend a procedure for the separation of the latter metal.

Manganese is precipitated from an ammoniacal tartrate solution with tannin. The precipitation is practically quantitative, and therefore it is necessary to separate manganese by precipitation as the sulfide before determining tantalum and columbium.[26]

Detection of tantalum and columbium. Tantalum and columbium may be detected by the colored complexes which they form with tannin. Columbium yields a reddish precipitate while tantalum yields a sulfur-yellow precipitate.

Moir [27] has used this reaction for the detection of tantalum and columbium in minerals:

Procedure. Fuse the finely powdered mineral with potassium hydroxide (not sodium hydroxide) and dissolve the melt in 20 parts of water. Filter immediately through a hardened filter paper in a Buchner funnel, and wash with warm dilute potassium hydroxide. Add an excess of cold hydrochloric acid and test the solution by adding an aqueous solution of tannin. When both tantalum and columbium are present, a reddish-brown precipitate is obtained.

Alimarin and Frid [28] have used a similar method for the detection of tantalum and columbium in minerals containing zirconium and titanium. This method is based upon the procedure of Schoeller and Waterhouse.[20]

Tannin may also be used as a confirmatory test in a systematic scheme of analysis.[91]

Detection of titanium. Tannin reacts with trivalent titanium to give a brick-red precipitate or a bright red color, and reacts with tetravalent titanium to yield an intense vivid red color.[1,29,30] By combining the treatment with tannin and 30 per cent hydrogen peroxide, the sensitivity of either reaction for titanium is strongly increased and may be used to detect as little as 0.05 mg. of titanium in 100 ml. of solution.[1]

Gapchenko and Sheintsis [31] have used the method of Moser, Neumayer and Winter [32] for determining titanium by means of tannin and antipyrine as the basis for a drop reaction for titanium:

Procedure. Saturate a strip of filter paper with a 10 per cent aqueous solution of tannin, place a drop of 20 per cent antipyrine solution on the paper, and then place a drop of the solution to be tested on the antipyrine solution. A red-brown color appears if titanium is present. The sensitivity of this reaction is 1 part of titanium in 250,000 parts of solution.

If iron, chromium, aluminum, cobalt, nickel, manganese, zinc, mercury, lead, copper, cadmium, zirconium, or bismuth are present, the colored spot on the filter paper is moistened with 1:4 sulfuric acid, which removes any coloration except that produced by titanium.

The only difficulty encountered in the above test occurs when molybdenum is present. With this metal a greenish-brown color is obtained, which is not entirely eliminated by treatment with sulfuric acid.

Determination of titanium. A red precipitate is obtained when tannin is added to oxalic or tartaric acid solutions containing titanium. Precipitation is quantitative when an excess of the reagent is added to a neutralized ammoniacal solution of the titanium salt.[6] Powell and Schoeller [33] have determined titanium by precipitating with a 4-5 per cent tannin solution from a neutralized oxalate solution which is half saturated with ammonium chloride. Zirconium remains in solution under these conditions, but uranium is precipitated along with titanium. If no ammonium chloride is present, only a partial precipitation of titanium occurs. The tannin complex with titanium is vivid red in color while the zirconium complex is white. This makes it possible to determine the completeness of the precipitation of titanium.

The following procedure is used for the separation of titanium from zirconium:

Procedure. Fuse the mixed oxides, containing an indefinite amount of zirconium, but not to exceed 0.1 g. of TiO_2, with potassium bisulfate in a silica crucible. Dissolve the mass in a saturated solution of ammonium oxalate containing 3 g. of ammonium oxalate. The volume should not exceed 150 ml. Heat to boiling and carefully titrate the solution with N ammonium hydroxide to the appearance of a faint cloudiness, and then immediately add the minimum quantity of N hydrochloric acid to render the solution clear. Add an equal volume of saturated ammonium chloride and continue boiling while adding dropwise a freshly prepared, filtered, 4-5 per cent tannin solution from a buret. Continue the addition of tannin until about 12 times as much has been added as there is TiO_2 present. Allow the mixture to stand on a hot plate until the flocculent red precipitate gathers into masses leaving the liquid clear. If the latter is orange-yellow in color, more of the reagent should be added. Precipitation is complete when the liquid is colorless or possesses only a pale straw-yellow tint. Digest on a hot plate for less than one-half hour and filter with moderate suction. Wash with a solution that contains 5 per cent of ammonium chloride and 1 per cent of ammonium oxalate and ignite while wet in a porcelain crucible (precipitate is designated as P′).

Test the filtrate for completeness of precipitation as follows: Heat to boiling and cautiously neutralize with N ammonium hydroxide, and then add the tannin solution dropwise until a slight precipitate is obtained. If the precipitate is dirty gray in color, titanium has been completely precipitated; but if the precipitate is yellow to pale orange in color some titanium is present and must be precipitated as described above and collected by filtration (this precipitate is designated as P′a).

The precipitates are collected and treated as follows: Weigh the precipitate accurately, fuse with potassium bisulfate, dissolve in a saturated solution containing 3 g. of ammonium oxalate, digest for a short time, filter, and submit the filtrate to the same procedure described above, except that the quantity of tannin used is 12 times that of the weight of the combined precipitates obtained above (P′ + P′a). Allow the precipitate to settle on a hot plate, filter with suction, test the filtrate for completeness of precipitation as described above, wash the precipitate and ignite and weigh as TiO_2. If the quantity of tannin precipitate is very large, transfer to a small beaker, carefully moisten and digest on a water-bath for one-half hour with 10-20 ml. of 0.5 N hydrochloric acid. Make the solution slightly ammoniacal, filter, wash, ignite and weigh.

Results obtained using the above method are shown in Table 16:

TABLE 16.—SEPARATION OF TITANIUM FROM ZIRCONIUM

ZrO_2 Taken g.	TiO_2 Taken g.	TiO_2 Found g.	Error g.	ZrO_2 Found g.
0.2006	0.0210	0.0214	+0.0004	0.2012
0.2073	0.0516	0.0522	+0.0006	0.2063
0.2001	0.0084	0.0086	+0.0002	0.1993
0.2042	0.0316	0.0325	+0.0009	0.2033
0.1060	0.0438	0.0446	+0.0008	0.1052
0.2096	0.0073	0.0072	—0.0001	0.2097
0.1532	0.0135	0.0133	—0.0002	0.1534
0.1221	0.0332	0.0337	+0.0005	0.1204
0.1306	0.0538	0.0534	—0.0004	0.1295

Das-Gupta[80] has also proposed a method for determining titanium by precipitating with tannin. Shemyakin[85] has used the following modification of Das-Gupta's method:

Procedure. Dilute 10 ml. of titanium chloride solution to 250 ml., heat moderately, and add 100 ml. of 2 per cent tannin solution and 30 ml. of 40 per cent ammonium acetate solution. Heat to boiling, allow to cool, and filter with suction. Wash the precipitate with 1 per cent ammonium acetate until the washings come through colorless. Dry the precipitate at 100-120° C. and ignite to TiO_2.

Titanium may be precipitated quantitatively by treating with a 10 per cent tannin solution and 20 per cent antipyrine in N sulfuric acid. This procedure is especially useful when titanium alone is to be determined and gives best results when the quantity of titanium ranges from 0.002 to 0.05 g. Excellent results, however, are obtained with quantities of titanium ranging as high as 0.1 g.:

Procedure. Add ammonium hydroxide to a solution of titanium sulfate or chloride until an excess is indicated by the odor of ammonia. Dissolve the precipitate which forms by adding 10 ml. of concentrated sulfuric acid, and add 40 ml. of 10 per cent tannin solution and dilute to 400 ml. Cool and stir well, and add a 20 per cent antipyrine solution until an orange-red, coarsely flocculent precipitate is obtained. Stop stirring, and add more tannin solution until a white curdy precipitate forms. Heat to boiling, remove the flame, and add 40 g. of ammonium sulfate. Cool and stir, and filter with suction. Wash the precipitate with a solution containing 100 ml. of water, 5 g. of concentrated sulfuric acid, 10 g. of ammonium sulfate and 1 g. of antipyrine. If alkali salts are present, wash the ignited precipitate with hot water, filter and again ignite.

Determination of uranium. Uranium is quantitatively precipitated by the addition of tannin to a neutralized tartrate solution containing ammonium acetate and ammonium chloride. It is also precipitated from an oxalate solution by tannin in the presence of a slight excess of ammonium hydroxide.[36] Das-Gupta[37-39] claims that for small quantities of uranium the tannin method is more reliable than the usual ammonium hydroxide precipitation, in which the presence of carbonates in the precipitant may cause low results. The method proposed by Das-Gupta consists of precipitating uranium by tannin from a neutralized acetate solution and igniting the dark brown tannin complex to U_3O_8.

Procedure. To 10-20 ml. of a neutral or faintly acid solution of a uranyl salt, containing the equivalent of 0.007-0.14 g. of U_3O_8, add 2 ml. of 2 per cent tannin solution for each 12 mg. of uranium present. A deep brown coloration appears. Heat to boiling, stir well, and add to the hot solution an ammoniacal 10 per cent ammonium acetate solution until the precipitate flocculates and the supernatant liquid is clear. Filter, wash with 2 per cent ammonium nitrate solution which has been made slightly ammoniacal, ignite and weigh as U_3O_8.

Uranic oxide, unlike the oxides of those metals which form pentoxides and dioxides, is attacked by dilute acids, and so for the digestion of the ignited tannin precipitate for the removal of traces of alkalies and sulfur trioxide,[36] the liquid should be made slightly ammoniacal prior to filtration.

Uranium is not precipitated by ammonium hydroxide from oxalate solutions, but a quantitative recovery of uranium is effected by means of tannin: [36]

Procedure. The slightly acid oxalate solution containing several grams of ammonium chloride is boiled and treated with a freshly prepared 2 per cent tannin solution and a slight excess of ammonium hydroxide. About 10 parts of tannin are added for each part of uranic oxide present. Allow the mixture to stand on a hot plate until clear, and then let stand for several hours at room temperature. Filter, wash the precipitate with a dilute solution of ammonium chloride, ignite and weigh.

The gross weight of the precipitate is almost invariably high due to contamination with silica derived from glass vessels in which the reaction is carried out. To correct this, the weighed oxide is dissolved in concentrated nitric acid, the solution evaporated to dryness, and the residue dissolved with hot water containing a drop of acid. The insoluble portion is collected, ignited, and weighed, and this weight is deducted from the gross weight of the precipitate. The difference represents the weight of U_3O_8.

Uranium is quantitatively precipitated by the addition of ammonium chloride and tannin to an ammonium carbonate solution containing pyridine. This property has been utilized for the separation of uranium from iron after the alkaline earths have been removed.[40,41]

Determination of tungsten. The action of tannin on tungstic acid is similar to that with columbium and tantalum in that it produces a voluminous colored precipitate. The recovery of tungstic acid from an acidified solution in the form of the bulky brown tannin complex is not quite quantitative. A few milligrams of tungsten remain in the solution as a colloidal suspension. By using cinchonine or another alkaloid the remaining tungsten is precipitated.[42] An alkali chloride is necessary for flocculation. The following procedure, using this principle, has been developed by Schoeller and Jahn: [42]

Procedure. Neutralize 100-150 ml. of an alkaline tungstate solution, containing an alkali chloride, with dilute hydrochloric acid to an end-point with phenolphthalein, and add a freshly prepared solution containing 0.5 g. of tannin. A part of the reagent may flocculate as a white precipitate if the chloride concentration is high. Continue the addition of dilute acid until the solution is acid to litmus, whereupon a brown turbidity due to the formation of the tungsten complex appears. Upon heating to boiling the precipitate becomes dark brown and flocculent. Boil gently for a few minutes and add 5 ml. of 5 per cent cinchonine hydrochloride diluted with water. Continue to boil for an additional 5 minutes, and allow the mixture to stand cold for at least 6 hours. Decant the liquid through a 9- or 11-cm; ashless filter paper. Mix the precipitate in a beaker with paper pulp and transfer to a filter. Wash thoroughly with a cold 5 per cent ammonium chloride solution containing a little tannin until all the alkali salt is removed. Dry the precipitate in a tared porcelain crucible, heat gently until completely charred, and then heat over a Bunsen flame until yellow and weigh as WO_3.

Results obtained using this method are given in Table 17.

TABLE 17.—DETERMINATION OF TUNGSTEN

WO_3 Taken g.	Weight of Precipitate (WO_3) g.	Error g.
0.0364	0.0359	—0.0005
0.0532	0.0536	+0.0004
0.0044	0.0047	+0.0003
0.0229	0.0233	+0.0004
0.0444	0.0443	—0.0001
0.0440	0.0443	+0.0003

Lambie [43] has studied the method of Schoeller and Jahn [42] and reports that it is more effective than that using cinchonine alone. Arnold [45] and Hinrichsen [46] have studied the use of tannin for the separation of tungsten and phosphorus and both report that the method is not satisfactory. More recently, however, Lambie [47] has proposed a method for the separation of tungstic and phosphoric acids which employs both tannin and cinchonine:

Reagent. Dissolve 50 g. of cinchonine in 500 ml. of 1:1 hydrochloric acid, dilute to 1 liter, and filter.

Procedure. Treat an alkaline solution containing not more than 0.2 g. of WO_3 with 50 ml. of a 20 per cent ammonium chloride solution, dilute to 200 ml., heat to 50° C., and add a freshly prepared tannin solution containing not less than 0.5 g. of tannin and 10 times as much by weight as WO_3 present. Acidify by the dropwise addition of 6 N hydrochloric acid with vigorous stirring, add filter paper pulp and then add the cinchonine solution with stirring. Use 5 ml. of this reagent for up to 0.1 g. of WO_3 and 10 ml. for 0.1-0.2 g. of WO_3. Filter, wash, and ignite and weigh as WO_3.

Moser and Blaustein [48] and others [44,96,97] have found that the substitution of antipyrine for cinchonine also makes precipitation complete. Lambie [96] reports that good recoveries of tungsten were obtained from solutions containing ammonium salts, sulfuric acid, alkali sulfates and phosphates. Precipitation of tungsten with tannin and antipyrine makes possible the separation of tungsten from the tri- and bivalent metals and from tin and silicic acid.

Procedure. To 200-300 ml. of a solution containing not more than 0.15 g. of WO_3, add 2-3 ml. of concentrated sulfuric acid for each 100 ml. of solution and add 5-8 g. of ammonium sulfate. Heat to boiling. To the boiling solution, add 3-4 times as much tannin as there is WO_3 present in the form of a 10 per cent aqueous solution, and boil the mixture gently for about 10 minutes. Allow to cool to room temperature, and add while stirring a 10 per cent antipyrine solution, using 1-1.5 g. of antipyrine for not more than 0.2 g. of WO_3. Filter and wash with a cold solution containing 5 ml. of concentrated sulfuric acid, 50 g. of ammonium sulfate and 2 g. of antipyrine per liter. Ignite in a porcelain crucible and weigh as WO_3.

This method gives satisfactory results in the presence of iron, aluminum, chromium, manganese, zinc, nickel and cobalt. The precipitate is sometimes impure, especially when iron and chromium are present, but it may be purified by dissolving in hot ammonium hydroxide, treating with an excess of sulfuric acid, and repeating the precipitation.

The following procedure is used for the separation of tungsten from stannic tin:[48]

Procedure. Add 1 mole of tartaric acid for each mole of WO_3 present, dilute the mixture to 500 ml. Make 1 N in hydrochloric acid and saturate the solution with hydrogen sulfide for 45 minutes. Filter off the precipitated stannic sulfide, and remove the excess hydrogen sulfide from the filtrate by boiling. Add a very small quantity of ferric chloride, a little 30 per cent hydrogen peroxide, and 3 ml. of concentrated sulfuric acid. Boil to destroy the tartaric acid and then precipitate tungsten with tannin and antipyrine. To accomplish this, it is necessary to dissolve the tungstic oxide which first forms by adding an excess of ammonium hydroxide and boiling. Then cool, make acid with sulfuric acid, and again boil. Precipitate in the usual manner.

The separation of tungstic acid from silica is carried out in a manner similar to that described above. With less than 0.1 g. of WO_3, some silica may be adsorbed. In this case it is necessary to treat the ignited WO_3 with hydrogen fluoride and sulfuric acid.

Determination of gallium. Gallium is only incompletely precipitated as $Ga(OH)_3$ by treating with ammonium hydroxide, but the precipitation is greatly facilitated by the presence of tannin.[49-51] According to Moser and Brukl[49] the best precipitant for gallium is the negatively charged tannin hydrosol, which adsorbs the positively charged gallium hydroxide which is produced by hydrolysis. Vlodavets[108] reports that the tannin method for determining gallium is as accurate as that with cupferron. The following procedure is recommended for the determination of gallium:[49]

Procedure. To a solution of a gallium salt which contains 1 per cent acetic acid, add sufficient ammonium nitrate to bring the content of that salt to about 2 per cent. Heat the mixture to boiling and to the boiling solution add dropwise a 10 per cent tannin solution until the precipitation is complete. A minimum of 0.5 g. of tannin should be used. The precipitate formed is so voluminous that not more than 0.1 g. of Ga_2O_3 can be conveniently handled.

About 1 g. of tannin is required to precipitate this quantity of gallium. Collect the precipitate on a filter and wash with hot water containing a little ammonium nitrate and a few drops of acetic acid. Dry, ignite and weigh as Ga_2O_3. The precipitate should not be ignited in platinum.

The above method makes possible an excellent separation of gallium from zinc, nickel, cobalt, manganese, cadmium, beryllium and thorium. By the use of tannin, 0.2 mg. of Ga_2O_3 per liter of solution is precipitated.

If the gallium solution contains a small quantity of free mineral acid proceed as follows:

Procedure. To the gallium solution containing very little free mineral acid, add ammonium acetate until its concentration corresponds to about 1 per cent of acetic acid. Then to each 100 ml. of solution add 2 g. of ammonium nitrate, heat to boiling, and proceed as described above.

To separate titanium and gallium, precipitate the former with tannin in the presence of ammonium oxalate and filter. Gallium is precipitated in the filtrate by adding a little ammonium hydroxide, more tannin, and then boiling.

Detection of gallium. Gallium can be detected by means of the complex which it forms with tannin, but Wenger and Duckert[52] who have studied the various methods for detecting gallium, do not recommend the use of this reagent. They report that tannin is of some interest as a gallium reagent but it is not as satisfactory as some others which have been proposed.

Determination of germanium. Davies and Morgan[53] have reported that tannin is an excellent precipitant for germanium, and that the tannin-germanium complex can be ignited to GeO_2. When suitable quantities of ammonium salts are present, germanium is readily precipitated by tannin as a colorless complex, even from solutions which are as much as 1 N in sulfuric acid. With nitric acid the maximum acidity is much lower, and the precipitate is finer in texture and more difficult to filter and wash.

In the absence of tantalum, columbium and molybdenum good results are obtained by the following procedure:

Procedure. To 150-250 ml. of a neutral solution containing about 50-60 mg. of GeO_2, add 5-15 ml. of 2 N sulfuric acid and 8-10 g. of ammonium sulfate. Heat almost to boiling. Add 10-30 ml. of a freshly prepared 5 per cent tannin solution slowly and with constant stirring. Allow to stand in a warm place until the precipitate has settled, and then filter through ashless filter paper, using gentle suction. Wash the precipitate with a 5 per cent ammonium nitrate solution containing 5 ml. of 2 N nitric acid per 100 ml. and a little tannin. Return the precipitate to the beaker with the wash liquid, stir with 50 ml. of this solution, and again filter. Again wash on the filter. Transfer the filter to a porcelain crucible, dry over a small flame, and ignite to GeO_2

The ignition may be carried out directly if carbonaceous matter is removed at a temperature below 700° C., but in general better results are obtained by oxidizing the tannin and paper by adding a few drops of sulfuric acid and successive portions of nitric acid. When most of the carbon has been removed, the residual acid is carefully evaporated and the residue ignited, cautiously at first, and finally at 1000° C.

Since germanium is precipitated by tannin from acid solutions it should be possible to separate this element from most elements except tungsten and possibly tantalum and columbium. Good results have been reported for the determination of germanium in binary mixtures containing germanium with arsenic or gallium, zinc, copper, iron, manganese, vanadium, titanium and zirconium. In the presence of arsenic, gallium, zinc, copper, iron and manganese the determination is carried out by the procedure described above; but when vanadium, titanium or zirconium is present, the determination is carried out by a modified procedure in which the acidity is increased as follows:

Procedure. Neutralize 250-300 ml. of the solution to be analyzed with 4-10 ml. of concentrated sulfuric acid and 8-10 g. of ammonium sulfate. Heat to boiling. Add dropwise with stirring, 10-20 ml. of 10 per cent tannin and then add 2-3 g. of ammonium sulfate dissolved in a little water. Cool, filter, wash, and ignite as described above.

Germanium and molybdenum cannot be separated satisfactorily by either of the above procedures due to co-precipitation. The results obtained in determining germanium in the presence of a number of other metals are given in Table 18.

Alimarin [100] has used tannin for the determination of germanium in coal ash and industrial wastes, and the same reagent has been applied to the estimation of germanium in steel.[101]

Detection of germanium. Germanium may be detected in the presence of other substances by converting to germanium chloride, dissolving in chloroform or carbon tetrachloride and precipitating as quinine tannate. This reaction is sensitive to 0.1γ of germanium.[102] For details of the test, see section on quinine.

Detection and determination of molybdenum. Molybdates in dilute acetic acid or neutral solutions yield a brown color or brownish precipitate with tannin.[1,54] This reaction will detect as little as 0.1 mg. of molybdenum in 100 ml. of solution. When a dilute solution of tannin is added to an acetic acid solution containing small quantities of molybdates a color is obtained, the intensity of which is proportional to the concentration of molybdate. This reaction has been used by Spurge [56] for the colorimetric determination of molybdenum. Not more than 2 per cent of molybdenum should be present if 1 g. of the sample is used. This method has also been successfully applied to aqueous solutions containing arsenic and bismuth.[56,84,87,88]

Procedure. Dissolve 1 g. of the sample in 10 ml. of concentrated nitric acid and heat gently for about 30 minutes. Evaporate to dryness on a water-bath and add 40 ml. of 1:3 hydrochloric acid and warm. If tungsten is present, filter. Add 15 ml. of concentrated ammonium hydroxide and boil for 5 minutes

TABLE 18.—SEPARATION OF GERMANIUM WITH TANNIN

Mixture Used			Found			
GeO_2 mg.	Other Substances Present	Mg. of Other Substances	GeO_2 mg.	Other Substances Found mg.	Vol. soln. ml.	Vol. 18 N H_2SO_4 ml.
24.9	As_2O_3	86.5	25.1	86.8	200	2
24.9	$ZnCl_2$	257.1	25.0	258	250	3
24.9	$CuSO_4 \cdot 5H_2O$	155.4	24.9	155.8	250	3
22.9	Ga_2O_3	27.3	23.2	27	200	2
28.1	Mohr's salt	124	28.0	124	200	3
28.1	$MnCl_2 \cdot 4H_2O$	66.	28.2	67.4	200	2
28.1	ZrO_2	28.4	28.0	28.8	250	4
31.2	V_2O_5	37.6	31.3	38.0	300	8
28.1	TiO_2	43.4	28.1	43.4	300	10

and filter immediately into a 250-ml. volumetric flask. Wash 3 or 4 times with small quantities of hot water. Wash the precipitate back into the original beaker, dissolve in 10 ml. of concentrated hydrochloric acid, and precipitate with 15 ml. of ammonium hydroxide. Filter into the volumetric flask containing the first filtrate, and again wash with water. Make the filtrate acid with acetic acid, and add 10 ml. of glacial acetic acid in excess. Cool, dilute to the mark, and mix thoroughly.

Place 2 ml. of freshly prepared 0.5 per cent tannin solution in each of two 50-ml. Nessler tubes and to one add 50 ml. of the sample and mix well. To the other tube add a standard solution with suitable amounts of distilled water until the color and the volume of the sample are duplicated. The quantity of molybdenum present should be such that the amount of standard required for the color comparison should not be less than 40 ml. due to the effect of dissolved salts and excess acid.

A standard molybdate solution is prepared as follows: Dissolve 9 g. of crystalline ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) in water and dilute to 1 liter. Standardize by precipitating a definite volume of this solution as lead molybdate, and converting the precipitate to lead sulfate. A quantity of 0.2106 g. of lead sulfate is equivalent to 0.1 g. of MoO_3. The solution should then be diluted to such concentration that each ml. contains 0.1 mg. of MoO_3. Measure a suitable volume of this solution into a flask, add 20 ml. of concentrated hydrochloric acid, dilute to about 100 ml. and add 30 ml. of concentrated ammonium hydroxide. Boil for 5 minutes, allow to cool, transfer to a 250-ml. volumetric flask and neutralize with acetic acid. Add 10 ml. of glacial acetic acid in excess, dilute to the mark and mix well.

Separation and determination of beryllium and aluminum. In a mixture containing not more than 0.08 g. of Al_2O_3 or BeO, aluminum is completely precipitated by tannin at a pH of 4.6, and no beryllium is precipitated if the pH of the solution is kept below 4.9. The amount of tannin used should be at least 12-15 times the weight of Al_2O_3 present. Beryllium may be precipitated in the filtrate by adding more tannin and making the solution more alkaline by the dropwise addition of ammonium hydroxide. Both the aluminum and the beryllium precipitates yield the corresponding oxides upon ignition.[60]

Moser and co-workers [61,62] were among the first to suggest the use of tannin for the separation and determination of beryllium and aluminum. Their separation was based on the difference of behavior of beryllium and aluminum when tannin is added to a dilute solution containing these metals and concentrated ammonium acetate. Aluminum is said to be quantitatively precipitated while beryllium remains in the solution. For the separation and determination of aluminum by this reaction it is necessary that both beryllium and aluminum be present as sulfates. The following procedure is described by Moser and Niessner: [62]

Reagent. Add 3 g. of tannin to 100 ml. of a cold saturated solution of ammonium acetate. This solution does not keep well, and should be freshly prepared. The solution should be perfectly clear, and possess at most a faint yellow color. A brown solution should be discarded.

Procedure. The solution to be analyzed should be made slightly acid with sulfuric acid, and should contain the metals as the sulfates. Dilute to 500 ml. with hot water if less than 0.1 g. of Al_2O_3 is present, or 600-800 ml. if more than 0.1 g. is contained in the sample. Warm the reagent solution to 80° C., and add all at once and with stirring to the diluted sample solution. Boil the mixture for 2 minutes, and remove the flame. Allow to stand cold until the aluminum precipitate has settled. Test for completeness of precipitation by adding a few more drops of the reagent.

If not more than 0.06 g. of Al_2O_3 is present, filter through black band filter paper, and wash with a warm 5 per cent ammonium acetate solution. Dry the paper and precipitate in an oven, and then ignite in a platinum crucible to Al_2O_3. Heat the residue 2 or 3 times with nitric acid to form pure white Al_2O_3.

If more than 0.06 g. of Al_2O_3 is contained in the precipitate, filter through a dense fritted glass crucible. Wash the precipitate with a warm 5 per cent ammonium acetate solution, and dissolve from the crucible with 1:3 nitric acid. Completely oxidize the tannin by adding a few drops of fuming nitric acid. The resulting solution should be completely colorless. Dilute the mixture, and precipitate aluminum as aluminum hydroxide. Filter, and ignite to the oxide.

This method has been criticized by several investigators [63,64] because the conditions of acidity of the solution from which the precipitation takes place are not definitely specified, and also because there is not sufficient difference in the acidity between the point of precipitation of the beryllium-tannin complex and the aluminum-tannin complex to make a clean separation possible.

In view of the conflicting statements which have been made regarding the applicability of tannin precipitation to the separation of aluminum and beryllium, Nichols and Schempf [60] have carefully studied the separation of aluminum and beryllium, and claim that excellent results are obtained by using the following procedure:

Procedure. Place the solution containing not more than 0.08 g. of Al_2O_3 or BeO in an 800-ml. beaker. If the aluminum or beryllium content of the unknown is greater than 0.08 g., use a suitable aliquot. To this solution add 25 ml. of saturated ammonium acetate, dilute to 500 ml. and adjust the pH to 4.6 with 6 N sulfuric acid and 1:1 ammonia. Heat to boiling, add slowly 50 ml. of 3 per cent tannin solution (at least 12-15 times the combined weight of the BeO and Al_2O_3), and digest on a steam-bath for 1 hour.

Cool the mixture to room temperature, filter the aluminum-tannin complex on a coarse-texture quantitative filter paper and wash thoroughly with a solution that has been adjusted to pH 4.6 and contains 5 per cent ammonium acetate and a little tannin. Dry the precipitate carefully in a covered platinum crucible and ignite and finally heat at 1200-1300° C. to constant weight. The loss of weight of the platinum during the ignition must be considered in the final determination. It is important that the pH of the wash solution be 4.6.

Beryllium is determined in the filtrate as follows:

Add a 3 per cent solution of tannin to the filtrate and washings from the aluminum separation until the amount of tannin added is 10-12 times the weight of the beryllium oxide. Heat to boiling and add 1:1 ammonium hydroxide cautiously drop by drop. A pale yellow precipitate of the beryllium-tannin complex forms as soon as the pH reaches 7.3, but ammonium hydroxide should be added until the solution is basic to litmus (pH 7.5). At this point remove the flame and allow the mixture to settle. Avoid an excess of tannin or of ammonium hydroxide.

Digestion of the precipitate is unnecessary. As soon as the precipitate has settled, filter on a coarse-grained quantitative filter paper, wash with a 5 per cent ammonium acetate solution containing a little tannin and made just basic to litmus. Dry and ignite to constant weight at 1200-1300° C., in a platinum crucible.

The precipitates of aluminum and beryllium should be white. If they are not, cautiously fume once or twice with a few drops of nitric acid before the final ignition.

The results obtained in separating aluminum and beryllium by the tannin method are reported by Nichols and Schempf [60] in Table 19.

The accuracy of the above method depends on the accurate control of the pH of the solution during the precipitation of aluminum. Sears and Gung [99] have described a modified method employing a mixed indicator which makes possible a convenient and accurate pH determination. The indicator consists of a mixture of 1 drop of 0.1 per cent methyl red and 6 drops of 0.1 per cent bromcresol green per 500 ml. of buffer solution employed by Nichols and Schempf. The color change is approached from the alkaline side.

Procedure. To the solution, diluted to 500 ml., and containing the buffer and indicator, add 1:1 ammonium hydroxide until the solution is blue-green in color, indicating a pH well above 5. Then add 6 N hydrochloric acid slowly and with stirring. The following color changes occur: blue-green, blue, purple, reddish-purple and red. The first appearance of the reddish-purple color coincides very closely with a pH of 4.6, which is the pH necessary for the complete separation of aluminum and beryllium.

The accuracy obtained using this method of control of acidity compares favorably with that of Nichols and Schempf.

Moser and Niessner [02] claim that large concentrations of chlorides make the separation of aluminum and beryllium impossible, but determination No. 8 in Table 19 was made in the presence of considerable quantities of chlorides.

Colbeck and co-workers [70] have used the method of Schoeller and Webb [3] for the precipitation of aluminum and chromium in the analysis of iron and steel.

Separation and determination of beryllium and iron. The following procedure is used for the separation of beryllium from ferric iron: [61]

Procedure. To a neutralized solution containing beryllium and ferric salts, add 30-40 g. of ammonium acetate and 20-25 g. of ammonium nitrate. Dilute to 400-500 ml., and for each 100 ml. of solution add 1.5 ml. of 80 per cent

TABLE 19.—SEPARATION OF BERYLLIUM AND ALUMINUM WITH TANNIN

	Al_2O_3 Used g.	Al_2O_3 Found g.	Error mg.	BeO Used g.	BeO Found g.	Error mg.
1	0.0124	0.0128	+0.4	0.0266	0.0264	—0.2
2	0.0247	0.0250	+0.3	0.0266	0.0268	+0.2
3	0.0493	0.0496	+0.3	0.0265	0.0268	+0.3
4	0.0740	0.0742	+0.2	0.0532	0.0531	—0.1
5	0.0740	0.0742	+0.2	0.0797	0.0799	+0.2
6	0.0124	0.0126	+0.2	0.0797	0.0797	0.0
7	0.0739	0.0739	0.0	0.0114	0.0112	—0.2
8	0.0247	0.0250	+0.3	0.0266	0.0268	+0.2

acetic acid. Heat to boiling and add a 10 per cent tannin solution with constant stirring until iron is completely precipitated. Since some of the ferric iron is probably reduced by the action of tannin, a few drops of 3 per cent hydrogen peroxide are added to the mixture just before the addition of tannin. Filter, and wash the precipitate with hot water. Dissolve the precipitate in hot dilute sulfuric acid, and repeat the precipitation of iron by adding ammonium acetate, ammonium nitrate and acetic acid. Wash the precipitate free of acid with water containing ammonium nitrate, dry, and ash carefully in a porcelain crucible. Fume with nitric acid and convert the precipitate to Fe_2O_3 by strong ignition.

Beryllium is determined in the filtrate after adding an excess of ammonium hydroxide.

Dixon[63] has studied the method used by Moser and Singer[61] for the separation of beryllium from titanuim and iron and offers some objections to the use of this procedure. He reports that it is doubtful if hydrogen peroxide can be employed in the presence of titanium; and when iron is present, the acidity of the solution must be reduced to such an extent that some beryllium is likely co-precipitated with the iron and also with titanium if the latter is present. Since a small quantity of iron usually accompanies the beryllium and titanium in the final stages of the analysis, it appears likely that the tannin method of separation may not be suitable.

Fresenius and Frommes[67-69] have used tannin for the determination of beryllium in steel, although they report that the 8-hydroxyquinoline method gives better results.

Separation and determination of beryllium and chromium. Beryllium is separated from chromium by a procedure similar to that employed with iron. Chromium is precipitated in the presence of about 2 per cent free acetic acid.[61]

Separation and determination of beryllium and titanium. The red titanium complex with tannin is insoluble in concentrated acetic acid. The following procedure may be used for the separation of beryllium from titanium:[61]

Procedure. To the acid solution containing titanium and beryllium add ammonium hydroxide dropwise to the appearance of a precipitate, and then add 16 g. of ammonium acetate, 20 g. of ammonium nitrate and 20-25 ml. of 80 per cent acetic acid. Heat to boiling and add a 10-fold excess of tannin in the form of a 10 per cent aqueous solution. Boil this mixture for a little while after the addition of tannin and then filter. Wash the red precipitate with a 10 per cent acetic acid solution containing ammonium nitrate. Dry, ash, fume with a little nitric acid, and ignite to TiO_2.

To determine beryllium, heat the filtrate to boiling with an excess of ammonium nitrate, and add an excess of 10 per cent tannin solution. Complete the precipitation by the dropwise addition of ammonium hydroxide. Filter, wash with hot water, dry at 110-130° C. and convert to BeO by igniting in a quartz crucible and fuming with nitric acid. Separation is complete with a single precipitation.

Separation and determination of beryllium and zirconium. Zirconium forms with tannin a white complex which is insoluble in acetic acid and 1:20 hydrochloric acid. Consequently, zirconium may be separated from beryllium under exactly the same conditions described for the separation of titanium from beryllium. Beryllium and zirconium are quantitatively separated by a single precipitation.[61]

Separation and determination of beryllium and thorium. Colloidal thorium hydroxide forms a flocculent white precipitate with tannin. This complex is insoluble in 2-2.5 per cent acetic acid in the presence of ammonium acetate. Thorium and beryllium may be separated by a double precipitation. The procedure is the same as that described for the separation of beryllium and iron.[61]

Separation and determination of beryllium and tungsten. An acidified solution of an alkali tungstate yields a deep brown, flocculent adsorption complex with tannin. This precipitate coagulates in the presence of an electrolyte, and after boiling for some time becomes easily filterable. Small quantities of tungsten are precipitated by considerable boiling, but with larger amounts, traces of the precipitate redissolve; the solution must stand for many hours on a water bath before they again precipitate.[61]

Procedure. Add 30-50 g. of ammonium nitrate and 10 ml. of sulfuric acid to the neutral or alkaline solution of the alkali tungstate and beryllium, and dilute to 300-500 ml. Heat the mixture to boiling, and add a 10 per cent tannin solution until a 10-fold excess is present. The excess is determined by the quantity of WO_3 present. Boil for 5 minutes, and add an additional 10 g. of ammonium nitrate, and then boil 5 minutes more. Filter and wash the precipitate with 1:10 sulfuric acid to which a little ammonium nitrate has been added. If the amount of tungsten present is fairly large, allow the filtrate to stand several hours on a boiling water bath. Filter through a small filter, and wash the precipitate with the above wash solution. Ash the combined precipitates in a porcelain crucible, fume with nitric acid, and ignite strongly to WO_3.

Moser and List [65] removed the last traces of tungsten from the filtrate after precipitating with tannin by adding a 15 per cent solution of antipyrine and heating on a water bath.

Separation and determination of beryllium and vanadium. Vanadium is precipitated by tannin from acetic acid solutions of alkali vanadates as a deep blue, voluminous complex. The tannin reduces a part of the vanadate to V_2O_4. The vanadium precipitate is practically insoluble in acetic acid, but is soluble in mineral acids. Precipitation is complete, although the filtrate obtained after the removal of the precipitate always has a greenish tint.[61]

Procedure. Dilute the solution of the alkali vanadate and beryllium to 400-500 ml. and for each 100 ml. of the resulting solution add 20 g. of ammonium acetate, 30 g. of ammonium nitrate and 2.5 ml. of 80 per cent acetic acid. Heat to boiling and precipitate vanadium with a 10-fold excess of 10 per cent tannin solution. The excess is calculated in relation to V_2O_5. Boil for several more minutes and filter hot. Wash with a 10 per cent ammonium acetate solution, and ash in a porcelain crucible. Heat with a few drops of nitric acid, and ignite until the residue melts. Weigh as V_2O_5.

Separation and determination of beryllium and molybdenum. This separation is not satisfactory because the adsorption compound is soluble in either acetic acid or ammonium hydroxide.

Separation and determination of beryllium and tin. Moser and List[65] have studied the separation of beryllium, and report that excellent results are obtained in separating beryllium and tin.

Procedure. Make the solution containing tin and beryllium chlorides strongly acid with hydrochloric acid and add 5 ml. of 10 per cent tannin solution, 10-20 g. of ammonium acetate and 10-20 g. of ammonium nitrate. Boil and allow the mixture to stand on a water-bath for 1 hour. Filter and wash with hot water containing ammonium acetate and a little tannin. If more than 0.2 g. of tin is present, dissolve the precipitate in hydrochloric acid and repeat the precipitation.

To determine beryllium, combine the filtrates and neutralize with ammonia, and evaporate to a small volume. Precipitate beryllium with tannin.

Separation of beryllium from columbium and tantalum. Schoeller and Webb[66] have reported that beryllium is quantitatively precipitated by tannin from an ammoniacal tartrate solution, but that tannin precipitation from an oxalate solution which is half saturated with ammonium chloride makes possible the separation of tantalum, columbium and titanium from beryllium as well as from zirconium, thorium, aluminum and uranium. In general it does not appear that tartrate and acetate solutions are suitable media for quantitative tannin separations.

Determination of zirconium. Under carefully controlled conditions zirconium is quantitatively precipitated by the addition of tannin. Zirconium may be determined quantitatively after the removal of columbium, tantalum and titanium by tartaric hydrolysis by a method described by Schoeller and Webb:[3]

Procedure. To the filtrate obtained from tartaric hydrolysis, add 1 g. of tannin in a concentrated aqueous solution, cool, and carefully titrate the mixture with 1:1 ammonium hydroxide. The end-point is determined by sticking a long strip of wet litmus paper to the side of the beaker so that the lower end is immersed in the solution. After titrating with ammonium hydroxide to the litmus end-point, make just acid (violet tint with the indicator) and boil for 2 minutes. The neutralization must be carried out with precision in order to obtain satisfactory results. Next add 5 g. of ammonium acetate, stir well, and allow to stand until the precipitate has settled. Collect the precipitate on a filter, and wash thoroughly with a 2 per cent ammonium chloride solution containing a little tannin. Ignite wet, and finally ignite at a high temperature, and then weigh as ZrO_2.

More recently, Schoeller[98] has recommended the following conditions for the precipitation of zirconium:

Procedure. To a solution of zirconium chloride, which must be free of sulfate and should not contain more than 0.1 g. of ZrO_2, add 20 ml. of a saturated solution of ammonium chloride. Dilute to 200 ml. and make 0.25 N with hydrochloric acid. The acid concentration should be 0.5 N if vanadium or thorium is present. Boil and add a freshly prepared solution containing 1 g. of tannin, and boil for 1 more minute. Cool, and allow to stand for 2 hours, and then filter with the aid of a little filter paper pulp. Wash the precipitate with a solution containing 50 ml. of saturated ammonium chloride and 25 ml. of concentrated hydrochloric acid in 500 ml. Measure the volume of wash solution used. Ignite the precipitate and weigh as ZrO_2.

To recover zirconium in the filtrate, add 7.5 N ammonium hydroxide until only 2-3 ml. of free acid remains (calculated from the volume of wash solution). Cool, filter, wash the precipitate and ignite as before.

This method gives a good separation of zirconium from the sesquioxides and monoxides of uranium, vanadium and thorium, but titanium and tin are precipitated with zirconium.

Determination of thorium. Neish[71] observed that thorium is quantitatively precipitated by means of tannin. Thorium can be determined by a procedure entirely similar to that described above for the determination of zirconium.[3]

Detection of cerium and the rare earths. Tannin gives color reactions with yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium and gadolinium, but the blue-violet color which occurs with cerium is specific and can be obtained with as little as 8γ of the metal. This is considerably more sensitive than the benzidine test for cerium. Herzfeld[72] has studied the reaction of tannin with the rare earths, and has used the following test:

Procedure. To the solution to be tested, add a 1 per cent solution of tannin in 50 per cent glycerol and 5 drops of a saturated solution of sodium acetate in 50 per cent glycerol. Allow the mixture to stand for 1 hour and observe the color of the Tyndall beam. The results obtained are shown in Table 20.

TABLE 20.—REACTION OF THE RARE EARTHS WITH TANNIN

Metal	Color of Tyndall Beam	Sensitivity
Yttrium	gray	8 γ
Lanthanum	gray	12 γ
Cerium	blue-violet	8 γ
Praseodymium	gray	8 γ
Neodymium	gray	12 γ
Samarium	gray	8 γ
Europium	yellow	8 γ
Gadolinium	gray	8 γ

Detection of iron. Iron salts react with tannin to give the well-known blue-black to black color. This reaction has long been known, and constitutes a sensitive test for iron, although it does not appear to be used at the present time for this purpose. According to Wagner [73] the color is obtained with 1 part of iron in 200,000 parts of solution. Fritz [74] has used this reaction in an electrospot method for detecting iron in metals.

Determination of copper. When heated with tannin, solutions of cupric salts yield light brown precipitates, but precipitation is not quantitative unless the solution is buffered with ammonium acetate. During the precipitation copper is reduced, and one mole of tannin combines with 10 equivalents of copper. Precipitation is quantitative in the presence of ammonium acetate but not in the presence of an excess of ammonia.[75]

Detection and determination of silver. Costeanu [76] has used tannin in a method for the determination of silver. Strips of filter paper are impregnated with a saturated solution of tannin and are then dried in air. A series of drops of silver nitrate, of known but different concentrations, are placed on each strip whereby a number of differently colored spots are obtained. These spots form a comparison series when arranged in order in increasing or decreasing intensity. The solution to be analyzed is diluted to a definite volume and a drop of this solution is placed on a strip of paper impregnated with tannin. The resulting spot is matched with that formed from silver nitrate of known concentration.

Detection of gold. A pale blue spot is obtained when filter paper that has been impregnated with tannin is treated with a solution containing a gold salt.[77]

A violet color is obtained when 1 volume of a 0.1 per cent solution of tannin is added to 10 volumes of a solution containing as little as 0.002 per cent gold chloride.[90]

Detection and determination of barium, calcium and strontium. Solutions of alkaline earth hydroxides give color reactions or colored precipitates with tannin.[93,94] Rosenthaler [78] has used this reaction for the detection of calcium, strontium and barium. When 1 ml. of a 1:10,000 solution of calcium, barium or strontium is mixed with 1 ml. of 1:1,000 aqueous solution of tannin and 2 drops of 0.1 N sodium hydroxide solution, a greenish color develops. A blank test should be carried out in making this test. The color may be bluish or bluish-green.

The following test is described by Lehrman and co-workers: [79]

Procedure. To 1-500 mg. of barium, strontium or calcium, add 1 ml. of 2 per cent tannin, and make alkaline by the addition of 6 N sodium hydroxide. Bluish-green solutions or precipitates are obtained depending upon the concentration of the ion. One mg. of barium, strontium or calcium can be detected in the presence of the alkali metals.

The ammonium ion interferes with this test, but this interference is eliminated by making the solution alkaline with sodium hydroxide, boiling off the ammonia and then proceeding as described above.

Ammer and Schmitz[80] have used the color reaction of tannin with the alkaline earths for the colorimetric determination of small quantities of these metals. When tannin is added to a dilute and slightly alkaline solution of a calcium, strontium or barium salt, or to mixtures of these salts, a yellowish-green color is developed which rapidly changes to blue, and after 3-5 minutes fades again to a yellowish color. At concentrations of less than 0.1 mg. of the metal per liter of solution, only the yellow color develops, and in solutions more concentrated than 100 mg. of the metal per liter a blue-green precipitate forms, making a dilution of the sample necessary. Because of rapid fading the color comparisons must be made rapidly. The method does not differentiate strontium, calcium and barium:

Procedure. Place 10 ml. of the neutralized solution containing calcium, strontium or barium, or mixtures of these three metals, in a Nessler tube and add 2 drops of 2 N sodium hydroxide and 1 drop of 10 per cent tannin solution. Shake and immediately compare the resulting color with that obtained similarly by treating solutions of known calcium, strontium or barium content.

The heavy metals interfere only when present in sufficient concentration to form precipitates with sodium hydroxide. Magnesium in concentrations greater than 5-10 mg. per liter or greater than 30 per cent of the strontium, calcium, and barium interferes in very dilute solutions by retarding the color development, and in more concentrated solutions by producing a white precipitate.

Detection of lead. A carmine-red color is obtained when an alkaline solution of a lead salt is treated with tannic acid. This reaction serves as a sensitive test for lead.[93]

Detection of ammonia. A mixture of silver nitrate and tannin is instantaneously reduced in the presence of ammonia to yield a silver mirror which may be used for the detection of ammonia.[81-83] The following procedure has been used by Makris[81] for the detection of ammonia:

Reagent. As reagent use a freshly prepared mixture of 2 ml. of 20 per cent silver nitrate solution and 1 ml. of a 5 per cent tannin solution.

Procedure. Place a drop of the mixture on a watch glass and bring close to 0.1 ml. of the solution to be tested. If ammonia is present, a ring of silver will form about the drop within a few seconds.

The above test may be modified by impregnating a piece of cotton with a few drops of the reagent and bringing it close to the mouth of a tube containing ammonia. When the tube is heated, a bright deposit of silver will form on the cotton if as little as 0.005 g. of ammonia is present.

Feigl[82] has used a similar test for the detection of ammonium salts. According to Feigl 0.1γ of ammonia can be detected at a concentration of 1:500,000. This method is not as sensitive, however, as that depending upon the formation of manganese dioxide in the presence of silver, which will detect 0.005γ of ammonia at a concentration of 1:10,000,000.

Determination of ammonia. Ammonia reacts with tannin in the presence of silver nitrate to give a yellow to orange or orange-red color. This reaction is more sensitive than the Nessler test and is equally convenient to apply. Makris [55] has used this reaction for the colorimetric determination of small quantities of ammonia in water:

Procedure. First prepare a standard solution of ammonia as follows: Dilute 1 ml. of a 10 per cent ammonia solution to 1 liter, and then dilute 100 ml. of this solution to 1 liter. One ml. of the standard contains 0.00001 g. of ammonia.

To 250-300 ml. of the water to be analyzed, add magnesium oxide and distill. Collect the first 50 ml. of the distillate in a flask of approximately 50 ml. content and use this for the determination. Arrange 10 cylinders of equal dimension, and to the first add 1 ml. of the standard, to the second add 2 ml., and so on until 10 ml. are added to the 10th cylinder. In this way a series of standards is obtained ranging from 0.01 mg. to 0.1 mg. of ammonia. To the first nine tubes add sufficient distilled water so that in all cylinders the water stands at the same height (total volume 10 ml.).

To 10 additional cylinders of the same dimension add 1 ml. of the distillate (solution to be analyzed) and 9 ml. of distilled water. To the first of the series of comparison tubes and to 1 of the 10 tubes containing the test solution, add simultaneously 2 drops of 5 per cent tannin solution and 1 drop of a 20 per cent silver nitrate solution. Compare the resulting colors within 1 minute. Repeat with the second tube of the comparison series and another of the tubes containing the unknown if the colors do not match in the first test. Repeat with other standards and other unknown solutions until the colors are the same. For more accurate results, a second series of comparison solutions may be prepared for the concentration interval between any two of the original standards.

The comparison must be made in the above test within one minute, since the color becomes much darker on standing.

Detection of thallium. A red solution changing to yellow is obtained when a solution containing thallium is treated with tannic acid and ammonia. This test is sensitive to 20 mg. of thallium per ml. of solution.[92]

Detection of sulfites. Rudnitzkii [34] has proposed a method for the rapid and easy detection of sulfites in the presence of thiosulfates and other anions which are normally present in the usual scheme of qualitative analysis.

Procedure. Make the solution neutral to phenolphthalein and add a dilute solution of tannin, a few drops of a 5 per cent solution of potassium chromate, and an excess of potassium ferrocyanide or a few drops of a 0.2 per cent solution of potassium ferricyanide. The appearance of a reddish or bluish violet color indicates the presence of sulfite.

The solution to be analyzed must be free of heavy metals and cyanides and the sulfite content must be at least 0.05 mg. per liter with potassium ferricyanide, and 0.2 mg. per liter with potassium chromate and potassium ferrocyanide solutions.

Detection of alkalinity. A mixture of equal volumes of alcoholic solutions of iodine and tannin produces a transient rose color in dilute solutions of any salt having an alkaline reaction. This color may be obtained with potassium carbonate at a dilution of 1:1 million. Sulfates and chlorides do not interfere with this test if present in small quantities. In concentrated solutions the rose color is masked by the formation of a brown color.[95]

Detection and determination of carbon monoxide. Normal blood when diluted with water and treated with tannin forms a gray suspension, but blood in which the hemoglobin is combined with carbon monoxide remains carmine-red under the same conditions. This reaction has been used for the determination of carbon monoxide both in blood and in air.[15,85-87]

The procedure for making this determination is described in detail by Snell.[88]

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TARTARIC ACID

Synonym: Dextrotartaric acid, dihydroxysuccinic acid

$C_4H_6O_6$ Mol. Wt. 150.09 Beil. Ref. III, 481.

$$HO_2C—CH(OH)—CH(OH)—CO_2H$$

Uses: Detection of ammonium, cerium, chromium, columbium, hydrogen peroxide, ozone, nitrite, potassium, strontium, tantalum, thallium and vanadium.

Determination of aluminum, cobalt, columbium, copper, molybdenum, nickel, potassium, silver, tantalum, tellurium, tungsten, zinc and zirconium.

Alkalimetric standard.

Tartaric acid is a white crystalline solid, having a strong acid taste. It melts at 169-171° C., and decomposes at a higher temperature with the odor of burnt sugar. One g. of the solid dissolves in 0.75 ml. of water, 3 ml. of alcohol, 1.7 ml. of methyl alcohol and 250 ml. of ether. It is insoluble in chloroform.

Neutralization and buffer action of tartaric acid. Tartaric acid is frequently used to neutralize bases and to prepare buffers in analytical procedures, but these uses are too extensive and varied to be discussed in detail. In general, such applications are to be found in text books devoted to methods of qualitative and quantitative analysis.

The formation of tartrate complexes. The heavy metal tartrates are difficultly soluble in water, but these dissolve more or less readily in neutral alkali tartrate solutions to form complex salts. The formation of these complex salts often serves to mask the reactions which are typical of the cations contained in them. For example, ammonium hydroxide causes no precipitation in solutions of iron, aluminum, titanium, chromium, antimony and tin tartrate complexes. Complex tartrate ions are also formed with manganese, cobalt, nickel, lead, copper, boron, molybdenum and other elements. The formation of these complexes constitutes the most important application of tartaric acid in analytical chemistry.

According to experiments by Curtman and Dubin,[90] 50 ml. of a solution containing 50 mg. of tartaric acid yields no precipitate with ammonium hydroxide unless at least 20 mg. of aluminum, 55 mg. of iron or 70 mg. of chromium is present.

Germuth [1] has studied the effect of pH upon the formation of certain compounds containing the complex ion of a number of metals and citric and tartaric acid. Samples of varying proportions of solutions containing definite quantities of iron, zinc, chromium, copper and aluminum were prepared and to each was added a quantity of tartaric acid slightly in excess of that required to form the complex ion. The pH range caused by a quantity of the acid sufficient to convert the metallic ion completely to the complex is shown in Table 21.

TABLE 21.—HYDROGEN ION CONCENTRATION OF SOLUTIONS OF COMPLEX IONS

(containing a slight excess of tartaric acid)

Cation	pH Range
Zinc	0.9-1.2
Chromium	1.4-1.6
Copper	0.8-1.1
Aluminum	4.5-4.8
Iron	0.6-0.8

By use of tartaric acid in a solution containing any of the above ions the pH need only be adjusted by the addition of the acid to the value given in order to prevent precipitation upon the addition of an alkali hydroxide.

Detection of potassium. In a neutral solution of a potassium salt, tartaric acid produces a white crystalline precipitate of potassium hydrogen tartrate. Potassium hydrogen tartrate is readily soluble in mineral acids, but is only slightly soluble in acetic acid and in water. At 10° C., 100 ml. of water dissolves 0.425 g. of the salt. The reaction is represented by the following equation:

$$K^+ + H_2C_4H_4O_6 \rightarrow KHC_4H_4O_6 + H^+$$

The reaction may be made more sensitive by adding sodium acetate to the reaction mixture to neutralize the hydrogen ions which are formed. Too much sodium acetate must be avoided, however, since the salt exerts a solvent action on potassium hydrogen tartrate.

The formation of slightly soluble potassium hydrogen tartrate has been widely used as a test for potassium.[6-11] The test originally proposed by Winkler [9] is carried out as follows:

Procedure. To 10 ml. of a neutral solution to be tested, and containing about 5 per cent of the salt, add 0.5 g. of crystalline sodium acetate and 0.5 g. of powdered tartaric acid. Shake vigorously. A clear solution results if potassium is absent. With as little as 0.2 per cent potassium, a crystalline precipitate forms immediately. A precipitate forms after 1-2 minutes with 0.1 per cent of potassium.

Ammonium, rubidium and cesium salts interfere with the potassium test by forming similar insoluble hydrogen tartrates.

This test often fails due to supersaturation. This difficulty may be eliminated in part by rubbing the walls of the test tube with a glass rod. Winkler [7] claims that the test always succeeds if tartaric acid is added in powdered form, probably due to the presence of traces of potassium hydrogen tartrate in the reagent.

Recklebeu [8] has modified Winkler's test as follows:

Procedure. Add to the solution to be tested a concentrated solution of sodium hydrogen tartrate. If a mixture of tartaric acid and sodium acetate is used, an excess of acid must be present. If upon rubbing the walls of the test tube, no crystallization occurs, transfer a drop of the solution to a watch glass and rub with a 10 per cent solution of a potassium salt until crystals form. Then transfer a few minute crystals to the test solution with a glass rod to induce precipitation of the potassium salt.

Scheringa [10] claims that sodium hydrogen tartrate reacts much more readily with potassium salts than either tartaric acid or tartaric acid buffered with sodium acetate.

Lutz [12] has studied the use of various reagents for the detection of potassium and claims that tartaric acid is one of the most sensitive. He reports a sensitivity of 1:1050. He further states that supersaturation can be overcome by adding a very small quantity of a solution containing 1 part of potassium nitrate and 99 parts of sodium nitrate.

Szebelledy and Jonas [13] recommend the use of racemic acid instead of dextro-tartaric acid, which is commonly used in the potassium test, since the former does not show such pronounced tendency for supersaturation. Tartaric acid and sodium tartrate may also be used for the microchemical detection of potassium,[11] although better results are claimed with sodium tartrate.

Determination of potassium. Various workers [14-25,27-33,35-45] have suggested the formation of slightly soluble potassium hydrogen tartrate as a basis for the determination of potassium. Of these, the procedures of Meurice [24] and Ajon [14] appear to be among the most promising. The method of Meurice depends upon the precipitation of potassium hydrogen tartrate from a solution containing a potassium salt by adding a saturated solution of sodium hydrogen tartrate in methyl alcohol. After standing overnight to complete the precipitation of potassium, the precipitate is filtered, washed, and dissolved in a measured volume of standard sodium hydroxide solution. The excess sodium hydroxide is then titrated with standard hydrochloric acid. The potassium is calculated from the amount of base used and the amount of standard acid required to neutralize the excess base. This method is reported to be moderately accurate for pure potassium sulfate, chloride or nitrate, and to be unaffected by moderate quantities of magnesium or calcium. The following is a modification of the Meurice procedure:

Procedure. To the solution containing about 1 g. of potassium chloride, or its equivalent, add an excess of sodium hydrogen tartrate until the acidity due to the excess reagent corresponds to 0.045-0.05 N. Then add an equal volume of 97 per cent methyl alcohol and allow the mixture to stand for one hour at 12° C. Allow the temperature to rise to 20° C., filter and wash with methyl alcohol diluted with an equal volume of water. Dissolve the precipitate of potassium hydrogen tartrate in an excess of standard sodium hydroxide and titrate the excess with a standard acid using phenolphthalein. One ml. of normal sodium hydroxide is equivalent to 0.0391 g. of potassium.

Daubner [29] has used a similar method for determining potassium in solutions containing no other salts except those of sodium and magnesium. Sodium, potassium and magnesium are converted to the sulfates and weighed together in that form; magnesium is then determined as magnesium ammonium arsenate, and potassium is determined by precipitating as above from a 50 per cent methyl alcohol solution. Sodium is obtained by difference.

Ajon [14] previously reported a method similar to that of Meurice [24] in which he precipitated potassium hydrogen tartrate from an ethyl alcohol solution. This method has also been used by Clarke and Davidson.[28] Potassium is precipitated as potassium hydrogen tartrate by the addition of a saturated solution of sodium hydrogen tartrate and 5 ml. of 20 per cent tartaric acid. The mixture is stirred mechanically for two minutes, after which alcohol is added to precipitate potassium. The precipitate is then filtered, washed with dilute alcohol and determined as described above.

Kunz [27] has proposed the use of aniline bitartrate as a precipitant for potassium. For the details of this use see section on aniline.

Marshall [20] has determined potassium by precipitating as potassium hydrogen tartrate and weighing in that form.

Procedure.. Evaporate the solution, or an aliquot containing about 50 mg. of K_2O, to dryness on a water bath and dissolve the residue in the least possible quantity of water. Usually 2-3 drops is sufficient. Cool the solution and add 20 ml. of 2 per cent tartaric acid in ethyl alcohol which has been shaken for several days with solid potassium hydrogen tartrate and filtered. After precipitation, add 10-20 ml. of a solution of potassium hydrogen tartrate in 96 per cent ethyl alcohol, and heat for 10 minutes on a water-bath. Allow to stand for 24 hours with frequent shaking. Filter through a weighed Gooch crucible, wash with more of the alcoholic solution of potassium hydrogen tartrate, and finally wash with 96 per cent alcohol. Dry at 80° C. and weigh as potassium hydrogen tartrate. This weight divided by 3.9992 gives the equivalent weight of K_2O.

The solution to be analyzed must contain the alkali metals as the chlorides, and other bases, silicates and phosphoric acid must be absent.

Fisk and Litarczek [87] have used a procedure in which potassium is titrated as the acid tartrate after precipitating as potassium cobaltinitrite. Koz'min [89] has modified the usual procedure by precipitating potassium as the hydrogen tartrate, and titrating the tartrate with potassium permanganate.

Wrobel [19] has used tartaric acid in a polarimetric method for determining potassium. When a solution containing sodium hydrogen tartrate and ammonium molybdate is treated with a potassium salt, the reaction of the latter with the tartrate results in a depression of the optical rotation of the liquid. By measuring the change in the optical rotation, the quantity of potassium present may be calculated.

Detection of ammonium salts. Tartaric acid reacts with ammonium salts to form a white crystalline precipitate of ammonium hydrogen tartrate. The addition of a little sodium acetate, and rubbing the walls of the glass vessel with a stirring rod hastens the formation of the precipitate. Ammonium hydrogen tartrate, like the corresponding potassium salt, is soluble in alkalies and mineral acids. It is possible to differentiate between the potassium salt and the ammonium salt by the difference in their behavior on ignition. When the potassium salt is heated, the residue obtained effervesces with hydrochloric acid, while upon ignition of the ammonium salt only carbon is left behind and this does not effervesce with acids. Further, ammonium hydrogen tartrate gives off ammonia when heated with sodium hydroxide solution.[46,47]

Detection of strontium. The use of sodium hydrogen tartrate as a microchemical reagent for strontium has been proposed, but Martini [48] claims this test to be inferior to others which have been used.

Determination of aluminum. Aluminum sulfate reacts with tartaric acid and its salts by the replacement by aluminum of hydrogen of the hydroxyl groups. The liberated sulfuric acid may be titrated with sodium hydroxide and phenolphthalein. The reaction is quantitative only if carried out at 100° C. Pavlinova [49-51] has used this reaction for the titrimetric determination of aluminum.

By the action of some salts on a mixture of an aluminum salt and an alkali metal tartrate, the acidity of the mixture is increased sharply and becomes equivalent to the amount of aluminum present. The aluminum content therefore may be determined by titration with a standard base in the presence of phenolphthalein:

Procedure. To 10 ml. of approximately 0.2 N solution, add 5 ml. of 10 per cent potassium tartrate or sodium tartrate and titrate with 0.1 N sodium hydroxide to a faint pink with phenolphthalein. Then add 40 per cent calcium chloride or strontium nitrate solution in such quantity that the concentration of the salt will be 2.5-3.5 per cent at the end of the titration. Again titrate with 0.1 N sodium hydroxide. From the increase in the acidity, the amount of aluminum present can be calculated.

Pavlinova [50] has used this method for the determination of aluminum in the electrolyte of chromate baths.

Determination of zirconium. Zolotukhin [52] has used a method similar to that proposed by Pavlinova [49-51] for the determination of zirconium.

Potassium fluoride reagent. Neutralize a solution of potassium fluoride to phenol red, and saturate with potassium chloride and potassium nitrate.

Procedure. To a known quantity of zirconium salt in aqueous solution, add an excess of sodium tartrate and titrate the cold solution with standard sodium hydroxide to an end-point with thymolphthalein.

In a separate portion of the zirconium solution, determine the free acid concentration by the potassium fluoride method as follows: to a known quantity of the zirconium salt, add the potassium fluoride solution, and then add potassium chloride or nitrate until saturated. Allow the mixture to stand 20 minutes, and titrate with sodium hydroxide to an end-point with phenol red.

The zirconium content is calculated from the amount of sodium hydroxide used for the titration of the acid equivalent to zirconium. This is obtained from the difference between the sodium hydroxide used for determining the total acidity (after the addition of sodium tartrate) and the free acid.

Separation of zirconium and titanium. Dittrich and Freund [53] have used tartaric acid in a procedure for the separation of titanium and zirconium. They claim that the separation of these metals with hydrogen sulfide in the presence of tartaric acid is satisfactory.

Separation of tin and antimony. Antimony dissolves in a mixture of nitric and tartaric acids to form a clear solution which contains complex tri- and pentavalent antimony compounds. Similarly, tin is dissolved at low temperatures by a mixture of nitric and tartaric acids, but the complex so formed is not stable and decomposes to form stannic acid on warming. The behavior of tin in the presence of antimony, however, is quite different: if an alloy or a mixture of antimony and tin is treated at 40-50° C. with nitric and tartaric acids, a clear solution is obtained, which may be heated to boiling without precipitation of stannic acid.[91] Tin is precipitated as the phosphate from this solution, and so separated from antimony.

Separation and determination of cobalt and nickel. Potassium iodide precipitates cobalt and nickel in an ammoniacal solution, and in the presence of tartaric acid, aluminum, chromium, iron, antimony and bismuth do not interfere. This behavior has been made the basis for a method for determining nickel and cobalt in the presence of iron, aluminum, chromium, antimony and bismuth.[2-5]

Procedure. Dissolve the material to be analyzed in nitric acid or hydrochloric acid, but if hydrochloric acid is used, convert the metals to the nitrates.

Evaporate almost to dryness, but avoid separation of the basic salts. Then add a quantity of tartaric acid equal to 10 times the weight of the trivalent metals present. The tartaric acid should be dissolved in a minimum quantity of water and added in the form of a solution. Add 50 ml. of concentrated ammonium hydroxide and 3-5 g. of solid potassium iodide according to the quantity of nickel or cobalt present. Stopper and allow to stand with occasional shaking for 15 minutes or longer. Filter, and wash with 4 per cent potassium iodide dissolved in 4 volumes of concentrated ammonium hydroxide and 1 volume of water. Dissolve the precipitate in dilute hydrochloric acid, filter, precipitate cobalt as the phosphate, and titrate nickel in the filtrate.

Copper, manganese, calcium oxide and magnesium oxide interefere.

Separation of tungsten and molybdenum. Tungstic oxide and sulfide are not precipitated from solutions of the soluble complex of tungstic acid and tartaric acid. This behavior makes possible the separation of molybdenum from tungsten.

Detection and determination of tantalum and columbium. Tartaric acid has extremely important applications in the analysis of tantalum and columbium (earth acids). When hydrochloric or nitric acid is added to a boiling tartrate solution of the earth acids, tantalic, columbic and tungstic acids are precipitated. This is known as "tartaric hydrolysis," which has been used by Powell, Schoeller and co-workers [54,55,57-59] in the analysis of the earth acids. For the details of these procedures, see section on tannin (page 145).

The following method may be used for the detection of tantalum and columbium: [55]

Procedure. Fuse approximately 0.1 g. of powdered mineral or oxide with 2 g. of potassium bisulfate in a silica crucible and dissolve the melt in a hot solution of 3 g. of tartaric acid in 10 ml. of water. Filter, if necessary, add about one-third volume of concentrated hydrochloric acid and boil. A white flocculent precipitate appears immediately, or after boiling a few minutes, if tantalum or columbium is present.

This reaction is specific for tantalum and columbium. Tungstic acid is also precipitated under the conditions of the above test, but the precipitate is yellow and is obtained only from a concentrated solution. The test is not affected by the presence of titanium oxide.

If the material contains considerable quantities of zirconium, the zirconium should be removed by treating the pyrosulfate melt with a hot 1 per cent tannin solution in 1.8 N sulfuric acid. After filtering the solution so formed, the residue is fused with bisulfate and subjected to the tartaric hydrolysis.

Detection of hydrogen peroxide. Tartaric acid has been used by Deniges [60-62] in a sensitive test for hydrogen peroxide.

Procedure. To 2 ml. of a 5 per cent solution of tartaric acid in a test tube, add 2 drops of a 5 per cent solution of ferrous ammonium sulfate and mix well. Add 1-2 drops of hydrogen peroxide, or 2 ml. if the peroxide solution is very dilute. Again mix and add 5-6 drops of sodium hydroxide solution. If hydrogen peroxide is present a violet coloration appears immediately. This test is given with a solution containing only 0.04 mg. of hydrogen peroxide.

Meigen and Schnerb [63,64] state that tartaric acid is catalytically oxidized to dihydroxymaleic acid by hydrogen peroxide in the presence of iron, copper, cobalt, nickel and lead. This reaction is useful in eliminating tartaric acid which has been added during an analytical procedure and which may later interfere with subsequent steps.[65-67]

Detection of vanadium. *p*-Phenetidine reacts very slowly with potassium chlorate or potassium bromate in dilute hydrochloric acid, but the reaction is catalyzed by as little as 1γ of vanadium. Potassium hydrogen tartrate activates this reaction.[68]

Detection of cerium. A brownish precipitate forms when sodium acetate and hydrogen peroxide are added to a neutral or acid solution of a ceric salt.[69] Wirth [70] has modified this reaction to use ammonium tartrate:

Procedure. To a neutral solution, add 5 ml. of 10 per cent ammonium tartrate solution and 5 ml. of dilute ammonium hydroxide and heat to boiling. If cerous salts are present, a yellow to yellowish-brown color appears. With concentrations of more than 0.1 per cent of cerous salts, the reaction occurs without heating. When hydrogen peroxide is added to the cerous tartrate mixture, a brown precipitate or a brown color is formed. The brown color appears with as little as 0.0002 per cent CeO_2.

Wenger and Duckert [71] do not recommend the reaction of Wirth [70] as a reagent for cerium, since a similar reaction is given with zirconium and thorium.

Detection of chromium and ozone. A solution prepared by dissolving 0.5 g. of α-naphthylamine and 50 g. of tartaric acid in 100 ml. of water is colored blue by the addition of a solution containing as little as 0.1 mg. of chromic acid in 100 ml. of water.[72]

A similar reagent is used for the detection of ozone, with which it yields a violet color.[73]

Determination of silver. Silver may be separated from antimony electrolytically by depositing the silver from a solution containing nitric and tartaric acids. Tartaric acid prevents the precipitation of antimony, and also decreases the resistance of the bath. The discharge potential of the silver from such a solution is about 0.3 volt higher than from solutions containing only nitric acid. Since tartaric acid is a reducing substance, it prevents the deposition of silver peroxide, and therefore makes unnecessary the addition of ethyl alcohol.[74,75]

Determination of zinc. Zinc may be deposited rapidly from a solution containing ammonium oxalate and free oxalic acid or tartaric acid.[76,77]

Zinc may be separated from nickel by depositing the zinc from an alkaline tartrate solution. After zinc is deposited, nickel may be determined by making the solution slightly acid with sulfuric acid, then adding an excess of ammonium hydroxide and electrolyzing.[78]

Determination of tellurium. Tellurium may be determined electrolytically by deposition from a solution of tellurous acid containing sulfuric acid and ammonium hydrogen tartrate. The solution should be heated to 60° C. and stirred during the electrolysis.[79]

Detection of thallium. Tartaric acid yields a white crystalline compound with thallous salts. This reaction has been used for the microchemical detection of thallium.[80,81]

Determination of copper. Interference by iron with the electrolytic determination of copper may be eliminated by the addition of tartaric acid.[82]

Detection of nitrite. Romijn[83] has proposed a reagent consisting of α-naphthylamine, sulfanilic acid and tartaric acid for the detection of nitrite.

Alkalimetric standard. Potassium, hydrogen tartrate has been recommended for the standardization of solutions of strong bases.[26,34,56,84-86,88] According to the U. S. Pharmacopoeia,[26] tartaric acid is purified for use as an alkalimetric standard as follows:

Procedure. Place 100 g. of potassium hydrogen tartrate in a beaker and mix with 85 ml. of water and 25 ml. of dilute hydrochloric acid. Cover the beaker and heat on a water bath with occasional stirring for about 3 hours. Cool quickly, decant off the supernatant liquid and wash the residue twice by decantation with 100 ml. portions of water. Filter, wash the residue with cold water until the filtrate no longer becomes opalescent upon treating with silver nitrate and a few drops of nitric acid. Dissolve the precipitate in the smallest possible volume of boiling water and filter. Cool the filtrate rapidly with stirring and filter when cold. Wash with 300 ml. of cold water, drain thoroughly and dry at 120° C. to constant weight.

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TARTRONIC ACID

Synonym: Hydroxymalonic acid

$C_3H_4O_5$ Mol. Wt. 120.06 Beil. Ref. III, 415.

$$\mathrm{HO_2C{-}CH(OH){-}CO_2H}$$

Use: Determination of aluminum.

Tartronic acid consists of colorless prisms which form with one-half mole of water when crystallized from an aqueous solution. The compound melts at 156-158° C. with decomposition. It is easily soluble in water, alcohol and ether, but is only sparingly soluble in ether when hydrated.

Preparation: Dissolve 5 g. of dihydroxytartaric acid (page 108) in the smallest possible quantity of water, and heat the solution at 80° C. until the evolution of carbon dioxide ceases. Cool, treat the crystalline mass several times with dry ether to remove impurities and unchanged dihydroxytartaric acid, and then dry the residue in a current of warm air.[1]

Determination of aluminum. Tartronic acid has been used by Pavlinova[2] in a titrimetric method for the determination of aluminum.

Procedure. Add tartronic acid to a solution of aluminum salt (containing no free acid) in such quantity that there is not less than one mole of the reagent to one atom of aluminum. Heat the resulting solution to 30-40° C. and titrate with 0.1 N of sodium hydroxide to the appearance of a pink color, using phenolphthalein as the indicator. An excess of tartronic acid does not interfere with the determination, but the solution must not be heated above 45° C. Three equivalents of sodium hydroxide are required for each atom of aluminum. The average error of this determination is 0.17-0.26 per cent.

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CHAPTER IV

AMINO ACIDS

1-AMINOANTHRAQUINONE-2-CARBOXYLIC ACID

$C_{15}H_9O_4N$ Mol. Wt. 267.22 Beil. Ref. XIV(702).

$$C_6H_4=(CO)_2=C_6H_2(NH_2)CO_2H$$

Uses: Detection of aluminum, magnesium and zinc.

This reagent is obtained as red needles from nitrobenzene. It melts at 286° C. It is easily soluble in aniline and boiling nitrobenzene, but is only slightly soluble in ether, benzene, and alcohol, and is quite insoluble in ligroin and water.

Preparation: Reduce 1-Nitroanthraquinone-2-carboxylic acid, prepared by the oxidation of 2-methyl-1-nitroanthraquinone,[1] to 1-aminoanthraquinone-2-carboxylic acid by shaking for 30 minutes with a freshly prepared solution of sodium sulfide on a boiling water bath. Saturate the resulting solution with hydrochloric acid, and extract the precipitate, which consists of the reagent and free sulfur, with a dilute sodium carbonate solution. Again precipitate with hydrochloric acid, dry, and recrystallize from 30 parts of boiling nitrobenzene.[2]

Detection of aluminum, magnesium, and zinc. 1-Aminoanthraquinone-2-carboxylic acid reacts with all cations except potassium, sodium, lithium, and ammonium to form red insoluble salts. Use may be made of these reactions for the microdetection of aluminum, magnesium, and zinc. Aluminum, magnesium, and zinc salts react with solutions of the potassium salt of the reagent to form dark red precipitates. This reaction is not characteristic.[3]

Reagent. The reagent is a 0.01 N solution of the potassium salt prepared by dissolving 0.266 g. of 1-aminoanthraquinone-2-carboxylic acid in 10 ml. of 0.1 N potassium hydroxide and diluting to 100 ml.

Procedure. Add a little of the reagent to 2 ml. of the neutral solution to be tested. A dark red precipitate is a positive test.

With this reaction 9γ of aluminum (1:220,000); 24γ of magnesium (1:83,000); and 0.65γ of zinc (1:3100) may be detected.

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m-AMINOBENZOIC ACID

$C_7H_7O_2N$ Mol. Wt. 137.13 Beil. Ref. XIV, 383.

$H_2N—C_6H_4—CO_2H$

Use: Detection of copper.

m-Aminobenzoic acid consists of a yellow powder or reddish crystals. An aqueous solution of the acid turns brown upon standing in air. The compound melts at 172-173° C. and is slightly soluble in water, but it is soluble in alcohol and ether.

Preparation: Mix 20 g. of *m*-nitrobenzoic acid, 40 g. of granulated tin and 120 ml. of concentrated hydrochloric acid in a liter flask and warm until the reaction begins. Allow the mixture to stand until the first vigorous reaction has subsided and then heat on a water-bath until the tin has dissolved. Evaporate the mixture on the water-bath until the hydrochloric acid is expelled, and then precipitate tin from the hot solution with hydrogen sulfide. Filter, wash the precipitate with hot water and evaporate the filtrate and washings to dryness. The free acid is obtained by dissolving a small portion of the residue in a very small quantity of water made alkaline with ammonia, and then acidifying with acetic acid. Purify by recrystallizing from water.[1]

Detection of copper. *m*-Aminobenzoic acid reacts with copper salts to give a yellowish-green spot. The test is obtained as a spot reaction on filter paper after drying the spot. This reaction will detect 1γ of copper in 0.025 ml. at a limiting concentration of 1:25,000.

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p-AMINOBENZOIC ACID

$C_7H_7O_2N$ Mol. Wt. 137.13 Beil. Ref. XIV, 418.

$H_2N—C_6H_4—CO_2H$

Use: Detection of copper.

p-Aminobenzoic acid is a yellowish-red crystalline solid. It melts at 186-187° C. It dissolves readily in boiling water, alcohol and ether.

Preparation: *p*-Aminobenzoic acid is prepared by the reduction of *p*-nitrobenzoic acid with tin and hydrochloric acid.[1,2]

Detection of copper. *p*-Aminobenzoic acid reacts with copper salts to give a yellowish-green compound which may be used for the detection of copper. The test is best carried out by spotting a strip of filter paper with a drop of a 0.2 per cent solution of the reagent and a drop of the copper salt solution, and then drying. This reaction serves to detect 10γ of copper.

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α-AMINO-*n*-CAPROIC ACID

Synonym: dl-Leucine

$C_6H_{13}O_2N$ Mol. Wt. 131.17 Beil. Ref. IV, 433.

$$CH_3(CH_2)_3CH(NH_2)—CO_2H$$

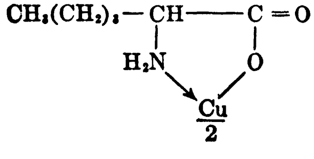
Use: Detection of copper.

This reagent is a white crystalline solid, melting at 275° C. It is soluble in 80 parts of water.

Preparation: *α-Bromo-n-caproic acid:* Place 200 g. of freshly distilled *n*-caproic acid in a liter flask with 96 ml. of bromine which has been dried by washing with 200 ml. of concentrated sulfuric acid. Add cautiously 3 ml. of phosphorus trichloride, fit the flask with a reflux condenser, and heat 5-6 hours in a water bath at 65-70° C. The condenser should be fitted with a trap and bottle containing water to prevent the escape of fumes. Towards the end of the reaction, raise the temperature to 100° C. Fractionally distill under diminished pressure, and collect the fraction boiling at 132-140° C./15 mm.

α-Amino-n-caproic acid: Place 844 ml. of concentrated ammonium hydroxide in a liter, round-bottom flask, and slowly add 150 g. of α-bromo-*n*-caproic acid. Stopper the flask and allow the mixture to stand 20-30 hours at a temperature of 50-55° C. Filter off the amino-acid with suction and wash with methyl alcohol.[1]

Detection of copper. α-Amino-*n*-caproic acid reacts with an aqueous solution of a copper salt to give a gray-blue precipitate of the following composition:



Kober and Sugiura [2] first observed this reaction and suggested its use for the detection of copper. The reaction has been further studied by Lyle, Curtman, and Marshall,[3] who propose the following test:

Reagent. Dissolve 0.67 g. of α-amino-*n*-caproic acid in 100 ml. of water. Heat to facilitate solution, and filter.

Procedure. To 1 ml. of the solution to be tested, add 1 ml. of 40 per cent sodium acetate, and 1 ml. of reagent. A gray-blue precipitate is a positive test for copper.

As little as 0.004 mg. of copper can be detected at a dilution of 1:333,000. Small amounts of iron do not interfere as in the ferrocyanide test. Mercury and zinc are the only common metals which yield precipitates under the conditions specified. Interference by mercury may be overcome by the addition of sodium chloride, and zinc may be prevented from precipitating by the proper adjustment of the acidity. Potassium cyanide inhibits the test. Ammonium salts, amines, and sodium citrate interfere.

This test is considered superior to the ferrocyanide test for copper, since iron does not interfere.

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3. W. G. Lyle, L. J. Curtman, and J. T. Marshall, *J. Am. Chem. Soc.* 37, 1471-81 (1915); *C.A.* 9, 1729 (1915).

3-AMINO-2-NAPHTHOIC ACID

$C_{11}H_9O_2N$ Mol. Wt. 187.18 Beil. Ref. XIV, 535.

$$H_2N—C_{10}H_0—CO_2H$$

Use: Determination of cobalt, copper, and nickel.

3-Amino-2-naphthoic acid is obtained as yellow leaves from alcohol. It melts at 214° C. It dissolves readily in alcohol and ether to form yellow solutions with a greenish fluorescence.

Preparation: 3-Amino-2-naphthoic acid is prepared by heating 1 part of sodium 3-hydroxy-2-naphthoate with 6 parts of 35 per cent ammonia to 260-280° C.[1]

Determination of copper, nickel and cobalt. Copper may be determined gravimetrically by the following procedure:[2]

Reagent. Dissolve 3 g. of 3-amino-2-naphthoic acid in 15.9 ml. of N sodium hydroxide and dilute to 100 ml. with water.

Procedure. Dilute 10 ml. of sample containing 0.03-0.04 g. of copper to 100 ml., heat to boiling, and add 15 ml. of reagent. Mix well, cool, filter through a sintered glass crucible (G4), and wash, first with a 0.01 per cent solution of sodium amino-naphthoate, and finally with alcohol. Dry at 130° C. for 30 minutes, cool, and weigh as $[C_{10}H_6(NH_2)CO_2]_2Cu$. The factor for copper is 0.1459.

Cobalt and nickel may be determined in a similar manner.

Excellent results are obtained with this procedure, but the precipitates with copper, nickel, and cobalt are very fine and difficult to filter. For this reason, precipitation with 3-amino-2-naphthoic acid is not very satisfactory. Anthranilic acid is more suitable as a precipitant.

1. R. Mohlau, *Ber.* 28, 3069 (1895).
2. R. J. Shennan, J. H. F. Smith and A. M. Ward, *Analyst.* 61, 395-400 (1936); *C.A.* 30, 5527 (1936).

4-AMINO-2-SULFOBENZOIC ACID

$C_7H_7O_5NS$ Mol. Wt. 217.19 Beil. Ref. XIV, 877 (769).

$HO_3S—C_6H_3(NH_2)CO_2H$

Use: Alkalimetric standard.

4-Amino-2-sulfobenzoic acid crystallizes from water as needles. It is very slightly soluble in cold water, and almost insoluble in alcohol and ether.

Preparation: Prepare the potassium salt of 4-nitro-2-sulfobenzoic acid by the sulfonation of *p*-nitrotoluene with fuming sulfuric acid, and oxidize with alkaline permanganate according to the method of Hart[1] and Kastle.[2] Dissolve the potassium salt of 4-nitro-2-sulfobenzoic acid in a considerable excess of concentrated ammonium hydroxide and saturate the solution with hydrogen sulfide. Evaporate to dryness on a water bath, and extract the residue with a small amount of water and filter. Acidify the filtrate with hydrochloric acid, collect the crystals, and recrystallize from boiling water containing animal charcoal.[3]

Alkalimetric standard. 4-Amino-2-sulfobenzoic acid has been proposed by Kastle[3] as a standard in alkalimetry. The compound is readily obtained in a pure state, and may be dried in air, with heat, or in a desiccator over sulfuric acid without change in composition. It is stable in air, and is not hygroscopic or deliquescent. It gives a sharp end-point with phenolphthalein. One drop of 0.1 N sodium hydroxide is sufficient to cause a color change. Results obtained using this reagent as a standard are accurate for practical purposes.

1. E. Hart, *Am. Chem. J.* 1, 349 (1879-80).
2. J. H. Kastle, *Am. Chem. J.* 11, 179 (1889).
3. J. H. Kastle, *Am. Chem. J.* **44**, 487-93 (1910); *C.A.* **5**, 846 (1911).

ANTHRANILIC ACID

Synonym: o-Aminobenzoic Acid

$C_7H_7O_2N$ Mol. Wt. 137.13 Beil. Ref. XIV, 310.

$H_2N—C_6H_4—CO_2H$

Use: Detection of cerium, cobalt, copper, lead, mercury, nitrite, palladium, silver, and uranium.

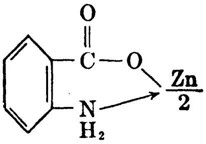
Determination of cadmium, cobalt, copper, lead, manganese, mercury, nickel, nitrite, and zinc.

Anthranilic acid is a white to pale yellow crystalline compound. It has a sweetish taste and melts at 144-146° C. It is sparingly soluble in cold water, but is quite soluble in hot water, alcohol, and ether. Alcohol, ether, and particularly glycerol solutions exhibit an amethyst fluorescence.

Preparation: Dissolve 40 g. of sodium hydroxide in 200 ml. of water and cool in a freezing mixture to −50° C., and then add gradually and with stirring

10.6 ml. (32 g.) of bromine. Mix 29.6 g. of phthalimide with water to form a thick paste and add to the bromine-sodium hydroxide solution. Remove the solution from the freezing mixture and allow to come to room temperature. Then stir in 24 g. of powdered sodium hydroxide and warm to 80° C. and filter. Cool the filtrate and add 110 ml. of concentrated hydrochloric acid until the liquid is neutral, and precipitate anthranilic acid by adding 30 ml. of glacial acetic acid. Filter, wash the precipitate with water, and dry in a desiccator. Crystallize from hot water with the addition of a little animal charcoal.[1-3]

The metal anthranilates. Anthranilic acid reacts with zinc, manganese, lead, mercury, cobalt, nickel, cadmium, and copper to form insoluble chelate compounds, which are suitable for quantitative determinations. These chelate compounds have a possible constitution represented by the following formula for the zinc compound:



The precipitation of zinc, cadmium, nickel, cobalt, manganese and copper by means of anthranilic acid from buffer solutions containing sodium acetate and acetic acid has been studied by Goto [27,28] to determine the most satisfactory pH range for the complete precipitation of the anthranilates. His results are given in Table 22.

TABLE 22.

Metal	Min. pH for Complete Precipitation	Max. pH at Which No Precipitation Takes Place
Zinc	4.72	3.76
Cadmium	5.23	4.25
Nickel	4.51	3.64
Cobalt	4.41	3.36
Manganese	5.15	4.10
Copper	2.79	1.40

From these results it may be seen that it is possible to precipitate copper alone from solutions of the above metals by proper pH control. It must be mentioned. however, that the anthranilates of zinc, cobalt, cadmium, and nickel are appreciably soluble in sodium acetate solutions.[29] The procedure of Funk and Ditt [15] for determining zinc, cadmium, cobalt, nickel, and copper in unbuffered neutral solutions gives excellent results, but the range of separations that can be accomplished under these conditions is very limited.

Those metals which are quantitatively precipitated by anthranilic acid may be determined either by drying and weighing the washed precipitate, or by titrating the anthranilic acid contained in the precipitate with a 0.1 N potassium bromide-potassium bromate solution. The titrimetric determination may be carried out either by the tribromination method of Day and Taggart[30] or by the dibromination method of Funk and Ditt.[31] According to the former method, a measured excess of standard potassium bromide-potassium bromate solution is allowed to react with anthranilic acid in the presence of hydrochloric acid to replace a part of the nuclear hydrogen by bromine. Potassium iodide is then added, and the liberated iodine determined by titrating with sodium thiosulfate. Funk and Ditt[31] dissolved the anthranilate precipitate in 4 N hydrochloric acid and titrated with a standard potassium bromide-potassium bromate solution, using a mixture of indigo carmine and styphnic acid as the indicator.

Ishimaru[25] and Kiba and Sato[26] have studied the drying temperatures of the metal anthranilates with the aid of the thermo-balance, and they recommend the following temperatures as most suitable when the metals are to be determined as the salts:

TABLE 23.

Metal	Drying Temperature ° C.	Determined as	Reference
Zinc	105-41	$Zn(C_7H_6O_2N)_2$	25
Cadmium	105-52	$Cd(C_7H_6O_2N)_2$	25
Cobalt	107-202	$Co(C_7H_6O_2N)_2$	25
Nickel	105-62	$Ni(C_7H_6O_2N)_2$	25
Copper	106-87	$Cu(C_7H_6O_2N)_2$	25
Manganese	100-20	$Mn(C_7H_6O_2N)_2$	26
Mercury	100-60	$Hg(C_7H_6O_2N)_2$	26
Lead	100-230	$Pb(C_7H_6O_2N)_2$	26

A suggested procedure for the gravimetric determination of the above metals is to precipitate as the anthranilates and then to convert to the oxides by fusion with anhydrous oxalic acid. The proper ignition temperatures for these salts have been determined by Ishimaru.[25] These are given in Table 24:

TABLE 24.

Metal	Ignition Temp. ° C.
Zinc	above 645
Cadmium	above 453
Cobalt	above 1005
Nickel	above 830
Copper	above 473

Determination of Zinc. In neutral or slightly acid solutions, zinc salts react with anthranilic acid to form a white crystalline precipitate of

$Zn(C_7H_6O_2N)_2$. Precipitation is quantitative, and is well adapted to the determination of zinc. A number of methods have been proposed for this determination,[4-7,12,36,37,42] but all involve essentially the same general procedure. The following method has been described by Funk and Ditt:[12]

Reagent. Dissolve 3 g. of pure anthranilic acid in 22 ml. of 1.0 N sodium hydroxide and filter. Dilute the pale yellow filtrate with water to 100 ml. Carefully add small quantities of anthranilic acid until the solution reacts very weakly acid to litmus. The solution has a light yellow color, which is not objectionable, but if the solution is brown it should be discarded. This solution keeps for several months if stored in a tightly stoppered bottle and protected from light.

Procedure. The solution to be analyzed should contain no more than a slight excess of acetic acid. Dilute to 150 ml. for each 0.1 g. of zinc, and precipitate in the cold by slowly adding 25-30 ml. of the reagent solution with stirring. Allow to stand 15 minutes until precipitation is complete, and filter through a porcelain filter crucible. Wash the precipitate with a solution prepared by diluting the reagent solution with 15-20 times as much water. Dry the precipitate with suction, and wash several times with alcohol to remove small quantities of sodium anthranilate. Remove the alcohol by suction, and dry to constant weight at 105-110° C. This requires about 30-45 minutes. The factor for zinc is 0.1937.

According to Mayr[41] and Cimerman and Wenger[42] this method gives values which are about 1 per cent too high. According to the latter investigators, this error may largely be eliminated by the proper control of such factors as the quantity of zinc, the volume of the solution, the pH of the reagent solution and test solution, the concentration and quantity of reagent, and the amount and concentration of the wash solution. Determinations carried out in a Pregl test tube, or in an Emich microbeaker give values accurate to within 0.3 per cent of the theoretical value.

The following procedure has more recently been recommended by Funk:[37]

Procedure. The solution to be tested should contain only a small quantity of mineral acid. If hydrochloric or nitric acid is present, evaporate the solution to a small volume to remove the volatile acid; or, if sulfuric acid is present, evaporate to dryness. Finally, dilute the material to 150 ml. The solution should contain about 0.1 g. of zinc. Heat to boiling and add 20 ml. of a 3 per cent solution of sodium anthranilate, and allow to stand for 15 minutes. Filter through a filter crucible, wash with a cold solution of the reagent that has been diluted 20 times with water, and dry at 105-110° C. The factor for zinc is 0.1937.

Potassium, sodium, ammonium, nitrate, chloride, and sulfate ions affect somewhat the accuracy of the determination, and should be present, if at all, only in small quantities.

Good results are obtained when the precipitation is carried out at 100° C., but this is not absolutely necessary in a procedure for the microdetermination of zinc.[38]

Cimerman and Wenger[4,42] recommended the following method for the microdetermination of zinc:

Reagent. Dilute 7 ml. of 1.0 N sodium hydroxide with a little distilled water, and add this solution to 1 g. of anthranilic acid. If the solid does not dissolve, add a little distilled water. Filter and adjust the pH to 5.5-5.6 with acetic acid. Dilute with distilled water to 1 per cent anthranilic acid. The pH is verified by using aliquot portions of the solution and suitable indicators. Store in a dark bottle, and protect from light.

Procedure. For the determination, use 2-5 ml. of the zinc solution, which should be neutral or very slightly acid with acetic acid (pH 5.5-7.0), and which should contain 1-3 mg. of zinc. Add dropwise the freshly prepared 1 per cent reagent solution until an excess of 0.3 ml. is present. Shake well, allow to stand 15 minutes, and filter through a small filter tube or filter stick. Wash once with 1-2 ml. of a 0.1 per cent reagent solution, and then wash 5-6 times with 1-2 ml. portions of alcohol. Dry 15 minutes at 110-115° C., allow to stand 15 minutes near the balance, then 5 minutes on the balance pan, and weigh in the 20th minute. The factor for zinc is 0.1937.

Exact results are obtained only if the excess reagent is limited to 0.3 ml. Thus, it is necessary to carry out a preliminary precipitation to determine the quantity of reagent needed. Theoretically, 0.46 ml. of the reagent solution is equivalent to 1.0 mg. of zinc. It is necessary to remember in the preliminary determination that the zinc value is about 1 per cent too high, and a correction for this error should be applied.

The precipitation of cadmium or zinc with anthranilic acid takes place in the presence of alkalies or alkaline earth metals without serious interference. Cobalt, nickel, copper, lead, and mercuric salts yield well crystallized, insoluble salts like those of zinc and cadmium, and are likely to interfere with their determination if present. Iron and copper may cause interference by co-precipitation. Iron causes no interference unless more than 10 mg. is present, but if more is present, it should be removed. Copper, however, may interfere even if present in minute quantity, since the sensitivity of the zinc and copper precipitation is about the same. Copper is satisfactorily separated from zinc by reduction to the metal with hydrazine hydrochloride in a sodium hydroxide solution. The copper is filtered off, and the zinc determined in the filtrate.[13]

Anderson[13] has recently described a method for determining zinc in a tin-lead solder when 0.08-4.7 mg. of zinc is present. The results are accurate to 2.5 per cent. Iron is separated by the basic acetate method, and copper by reduction with hydrazine hydrochloride. This method has also been used for white metal alloys, zinc chloride fluxes, enamel coating of tin cans, and synthetic mixtures.

A titrimetric method for determining zinc has been based on the fact that one molecule of anthranilic acid in acid solution reacts with 6 atoms of bromine; thus, by determining the quantity of bromine used in reacting with the anthranilic acid contained in the zinc precipitate, the amount of zinc present may be indirectly estimated. One atom of zinc corresponds to 8 atoms of bromine.[12]

Procedure. Precipitate zinc anthranilate as described above, wash well, and dissolve in 4 N hydrochloric acid. Transfer the solution to a glass-stoppered bottle, and titrate with a standard bromide-bromate solution. As the indicator, use a solution containing 0.2 g. of indigo carmine and 0.2 g. of styphnic acid in 100 ml. of water. Continue the titration until the indicator changes from green to yellow. Then add immediately several ml. of 0.2 N potassium iodide solution, dilute with water, and titrate the liberated iodine with standard thiosulfate, using starch as the indicator. 1 ml. 0.1 N $KBrO_3$ = 0.8173 mg. zinc.

Determination of cadmium. Anthranilic acid reacts with solutions of cadmium salts to form a white crystalline precipitate of $Cd(C_7H_6O_2N)_2$. Precipitation of cadmium is quantitative and is well adapted to the determination of cadmium. The determination procedure is entirely similar to that described for zinc.

Excellent results are obtained by the method of Wenger and Masset.[5]

Procedure. Heat to boiling a solution containing 1-3 mg. of cadmium at a pH of 6, and containing no hydrochloric acid or acetic acid. Add 0.55 ml. of a freshly prepared 2 per cent solution of sodium anthranilate. Stir well and allow to cool completely. Filter, and wash twice with one ml. of 96 per cent ethyl alcohol, and finally dry at 135-140° C. and weigh. The factor for cadmium is 0.2923.

Three separate techniques have been employed for this determination: the first by Schwartz-Bergkampf,[9] using a filter-beaker; the second by Emich,[10] using a filter rod; and the third by Pregl,[11] using a filter tube. All give good results.

Cadmium may also be determined by a titrimetric method similar to that used for zinc. One ml. of 0.1 N $KBrO_3$=1.4003 mg. of cadmium.

Separation of zinc from cobalt, nickel and manganese. Zinc may be separated satisfactorily from cobalt, nickel and manganese by precipitating the zinc with anthranilic acid according to the method of Funk and Ditt.[12] There is a tendency toward co-precipitation in solutions containing cobalt, but this is prevented by adding 5 ml. of 4 per cent acrolein solution for each 0.05 g. of zinc oxide.[14]

Detection and determination of cobalt. A red precipitate corresponding to the formula $Co(C_7H_6O_2N)_2$ is obtained when sodium anthranilate is added to a slightly acid or neutral solution of a cobalt salt. The formation of the precipitate may be used as a qualitative test for cobalt; or, since precipitation is quantitative, the reaction may be used for the estimation of cobalt. By means of this reaction 0.006 mg. of cobalt in 5 ml. of solution may be detected.[15,36] Cobalt is determined by the following procedure:

Procedure. The solution of the cobalt salt should contain no free acid, and should have a volume of 250 ml. for 0.1 g. of cobalt. Heat this solution to boiling and add 15 ml. of the 3 per cent sodium anthranilate solution prepared as described for the determination of zinc. For quantities of cobalt less than 0.1 g., the volume of solution and reagent should be proportionately smaller. Boil gently for 5 minutes after adding the reagent, and then let stand 5-10 minutes. Filter while still hot through a porcelain filter crucible. Wash cold with a solution prepared by diluting 5 ml. of the reagent solution with 95 ml. of water, and then wash several times with alcohol. Suck as dry as possible, and dry at 105-110° C. to constant weight. The factor for cobalt is 0.17803.

The practical application of this method appears to be limited, since many metals such as iron, nickel and zinc interfere and must be removed.

Wenger, Cimerman and Corbaz [16,17] have developed the following method for the microdetermination of cobalt:

Reagent. Dissolve 0.2 g. of anthranilic acid in 1.6 ml. of 1.0 N sodium hydroxide and dilute with 8 ml. of distilled water. Filter, and make the pH 6 by adding 6-7 drops of 5 per cent acetic acid. The resulting solution is a 2 per cent sodium anthranilate reagent.

Procedure. Place 2 ml. of a neutral or slightly acid solution to be analyzed, containing 0.1-4.0 mg. of cobalt, in a Jena microfilter beaker, and heat in a copper block to 170° C., and then add the reagent dropwise to complete precipitation.

The quantity of reagent added is determined by the amount of cobalt present: for 1.0-4.0 mg. of cobalt, use 0.5 ml. of the reagent solution for each milligram of cobalt; for 1.0-0.2 mg. of cobalt, use 0.16-0.2 ml. of the reagent solution for each 0.1 mg. of cobalt; and for quantities of cobalt less than 0.2 mg., use 0.3-0.4 ml. of reagent for each 0.1 mg. of cobalt.

Shake well after the addition of the reagent, and heat to boiling. Allow to stand 10 minutes and filter. Wash once with 2 ml. of 0.2 per cent sodium anthranilate solution, and then twice with 1-ml. portions of alcohol. Dry at 120-130° C. in a current of dust-free air for 15 minutes. Cool and weigh. The factor for cobalt is 0.17803.

The maximum error using the Pregl [11] or the Emich [10] technique is ±0.33 per cent. The method of Schwartz-Bergkampf [9] is the simplest and that of Pregl the most difficult. The method of Schwartz-Bergkampf is recommended for quantities of cobalt ranging 0.1 to 4.0 mg.; that of Emich for 1.0-4.0 mg.; and that of Pregl for amounts greater than 4.0 mg.[18]

Relatively large amounts of sodium chloride and moderate quantities of ammonium chloride do not affect the results, but sodium acetate must be absent. Acid solutions of cobalt must be neutralized with sodium carbonate to turbidity and then cleared with 1-3 drops of 1:200 hydrochloric acid. Excessive amounts of acid must be removed by evaporation.[19] Ions such as nickel, copper, zinc, cadmium, lead, and mercuric, which also precipitate with the reagent, must be absent.

Cobalt may be determined as the anthranilate after separating from nickel with dimethylglyoxime. After precipitation with the latter, filter, and to the filtrate add sulfuric acid and evaporate to fumes. Dilute with water, and precipitate cobalt with a 3 per cent solution of sodium anthranilate.[20]

Cobalt may be determined by a titrimetric method similar to that used for zinc. One ml. of 0.1 N $KBrO_3$ solution=0.7368 mg. of cobalt.

Detection and determination of copper. A green precipitate of copper anthranilate, $Cu(C_7H_6O_2N)_2$, is formed when anthranilic acid or sodium anthranilate is added to a hot neutral solution of a cupric salt.[15,36] A test may be obtained with a solution containing 0.005 mg. of copper in 5 ml. of solution. Precipitation is quantitative, thus serving as a method for the estimation of copper.

Procedure. Adjust the volume of the solution to be analyzed to 200 ml. for each 0.05 g. of copper, and make neutral or very slightly acid with acetic acid. Heat to boiling, remove the flame, and precipitate by adding 12.5 ml. of 3 per cent sodium anthranilate solution for each 0.05 g. of copper. Allow the mixture to stand for several minutes and filter while still hot through a filter crucible. Wash with a solution prepared by adding 1-2 ml. of the precipitating reagent to 100 ml. of hot water. Dry to constant weight at 105-110° C. and weigh. The factor for copper is 0.1838.

The washed precipitate may be dissolved and titrated with a bromide-bromate solution, but the procedure is different from that described in the section on zinc because of the reaction between cupric ions and iodides. The titration is carried out as follows: dissolve the copper salt in 4 N hydrochloric acid and titrate with the bromide-bromate solution until the styphnic acid-indigo carmine indicator (page 197) just changes to yellow. Then add a small quantity of standard arsenic acid solution, a little more of the indicator, and again titrate with bromide-bromate solution until the indicator changes to green. One ml. of 0.1 N $KBrO_3$ solution is equivalent to 0.7946 mg. of copper.

In carrying out the microanalysis by the Pregl method, it is advisable to neutralize the solution after precipitating copper with anthranilic acid. There should never be more than 2 mg. of copper used in the analysis. An excess of exactly 30 per cent of the reagent is recommended, since the precipitate is always contaminated if a greater quantity is used, and the adsorbed reagent cannot be removed from the precipitate by washing with alcohol or ether.[39]

Pozzi-Escot [21] has used the blue crystals which are formed in the reaction between copper sulfate and anthranilic acid for the microchemical detection of copper.

Determination of nickel. Anthranilic acid yields a light green precipitate of $Ni(C_7H_6O_2N)_2$ when added to a hot neutral solution of a nickel salt. A test may be obtained using this reaction with solutions containing as little as 0.011 mg. of nickel in 5 ml. Since precipitation is quantitative, this reaction is also used for the determination of nickel.[15]

Procedure. Adjust the volume of the solution to be analyzed to about 300 ml. for each 0.1 g. of nickel, and make neutral or only very slightly acid with acetic acid. Heat to boiling and add dropwise and with stirring 25 ml. of a 3 per cent solution of sodium anthranilate (page 195). Boil gently for 5 minutes, and allow to stand 10 minutes, and then filter through a porcelain filter crucible. Wash once with 2 ml. of 0.2 per cent sodium anthranilate solution, and twice with 1-ml. portions of alcohol. Dry to constant weight at 105-110° C. and weigh. The factor for nickel is 0.17742.

Nickel may be determined by a titration procedure after precipitating as nickel anthranilate.[36] The determination is carried out exactly as described for zinc with this modification: it is better to dissolve the nickel precipitate in hot, concentrated hydrochloric acid and then dilute with water. One ml. of 0.1 N $KBrO_3$ = 0.7336 mg. of nickel.

Detection and determination of lead. Although the lead salt of anthranilic acid is more soluble than the corresponding copper and zinc salts, it is sufficiently insoluble to be used for the determination of lead. With 1 ml. of 10 per cent reagent, 0.05 mg. of lead in 5 ml. of solution gives a distinct turbidity within 10 minutes. The insoluble compound has the formula $Pb(C_7H_6O_2N)_2$. The following procedure is recommended by Funk and Römer:[22]

Procedure. To 100 ml. of solution containing 0.1 g. of lead, add 30 ml. of 3 per cent sodium anthranilate solution (page 195). The sample solution should be cold and practically neutral. Allow to stand 1 hour or longer, and filter through a filter crucible. Wash by suction with a solution prepared by diluting the precipitating reagent 5-6 times with water. Finally, wash with a little alcohol, dry at 105-110° C. to constant weight and weigh. The factor for lead is 0.4323.

The washed precipitate may be dissolved in hot, 10 per cent ammonium acetate solution, cooled, acidified with hydrochloric acid, and titrated with a standard bromide-bromate solution.

Ions which form insoluble salts with anthranilic acid interfere with the lead determination, but lead may be separated from many interfering ions by precipitation from a nitric acid solution with thiourea.[23]

Procedure. Add nitric acid to the solution containing lead until the concentration of the acid is 1-2 N, and add an equal volume of saturated thiourea in 1.0 N nitric acid. Cool in ice water and filter. Wash the precipitate with an acid solution of thiourea, and dissolve the washed precipitate in hot water. Lead is determined in this solution with anthranilic acid according to the above procedure.

The thiourea precipitate is $2Pb(NO_3)_2 \cdot 11CS(NH_2)_2$. Complexes of other ions are more soluble in dilute nitric acid and are not precipitated.

Determination of mercury. Mercury, like lead, forms a precipitate with anthranilic acid, but the corresponding mercury salt is not stable in the presence of alkalies or ammonium chloride. Consequently, the mercury precipitate must not stand long before filtering. Further, results are much too low if the precipitation takes place in a hot solution. Good results may be obtained, however, by using the following procedure: [22]

Procedure. To a neutral solution of mercuric nitrate, containing 0.1 g. of mercury in 200 ml., add 10 ml. of a 3 per cent solution of sodium anthranilate. Filter *immediately,* and wash promptly, first with the 3 per cent reagent diluted with 20 volumes of water, and finally with a little alcohol. Dry at 105-110° C. and weigh. The factor for mercury is 0.4237.

Determination of manganese. Manganese anthranilate is more soluble than the corresponding salts of zinc, copper, cadmium, and lead, but it is still sufficiently insoluble to be used for the gravimetric or titrimetric determination of manganese. The volume of the solution used in the determination should not exceed 80 ml. for 0.1 g. of manganese, and 60 ml. of a 3 per cent reagent is suitable for the precipitation. For washing, use 50-60 ml. of 0.5 per cent reagent, followed by alcohol. Satisfactory results are obtained even in the presence of barium, strontium, magnesium, calcium, and considerable amounts of ammonium salts.[24]

Detection of cerium. Ammonium anthranilate reacts with solutions of ceric compounds to give an abundant, dark-red precipitate, which is insoluble in acids, but which turns brown when treated with ammonium hydroxide. Solutions of trivalent cerium, thorium, titanium, zirconium, praseodymium and columbium do not give this test. This reaction has not proved sufficiently sensitive to be used as a spot test.[32]

Detection of uranium. Uranium may be detected by a microchemical reaction.[33]

Procedure. Evaporate a drop of the solution to be tested to dryness, add a drop of a saturated solution of anthranilic acid, and then examine under a microscope. The formation of needle-shaped prisms, often collected in druses, and differing from the crystals of anthranilic acid, indicates the presence of uranyl ions.

The size of the crystals ranges from 25 to 40μ. The sensitivity of the reaction is 0.012γ. Copper, silver, and zinc interfere. However, it is possible to detect 0.068γ of uranium in the presence of a 20-fold amount of copper, a 40-fold amount of silver, and a 15-fold amount of mercury, all present in the same solution.

Microchemical reactions. Copper, mercurous, palladium, zinc, and silver ions form characteristic precipitates with anthranilic acid.[34]

Procedure. Place one drop of the salt solution and one drop of 0.5 per cent anthranilic acid solution on a glass slide and heat gently. Examine the crystals with a microscope.

The results are given in Table 25.

TABLE 25.

Metal	Description of Crystals	Cryst. Size	Sensitiveness
Copper	Pale green hexagons and prisms	30-40 μ	0.013 γ
Mercury	Colorless needles	200 μ	0.060 γ
Palladium	Yellow granules	5-10 μ	0.015 γ
Zinc	Colorless rhombs	80-100 μ	0.050 γ
Silver	Needles and prisms	100-50 μ	0.240 γ

Cobalt, ferric and ceric ions form amorphous precipitates. No other cations precipitate under the conditions of the test.

Detection and determination of nitrite. Anthranilic acid may be substituted for sulfanilic acid in the diazotization method for detecting and determining nitrites. There are certain advantages in the use of anthranilic acid: it is not difficult to obtain the pure compound; its purity may be tested by melting point determination; the end-point of the reaction is sharp; and the diazo compound is stable.[35]

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5-BROMO-2-AMINOBENZOIC ACID

Synonym: 5-Bromoanthranilic Acid

$C_7H_6O_2NBr$ Mol. Wt. 216.04 Beil. Ref. XIV, 370(551)

$$Br—C_6H_3(NH_2)CO_2H$$

Use: Determination of cobalt, copper, nickel and zinc.

5-Bromo-2-aminobenzoic acid is a crystalline solid. It melts at 218-219° C. It is very slightly soluble in water, moderately soluble in alcohol, ether, chloroform, benzene and acetic acid, and is very soluble in acetone.

Preparation: Dissolve 25 g. of anthranilic acid in 250 ml. of glacial acetic acid, and cool to 15-16° C. Add slowly 29.4 g. of bromine at such rate as to prevent an increase in the temperature of the reaction mixture. Filter and wash the precipitate with benzene. Boil the residue with 500 ml. of water containing 25 ml. of concentrated hydrochloric acid and filter with suction. Extract the insoluble residue twice more with 500 ml. of water. The filtrates upon cooling yield crystals of the reagent.[1,2]

Determination of copper, cobalt, nickel and zinc. 5-Bromo-2-aminobenzoic acid reacts with solutions of salts of most of the heavy metals to yield precipitates, but no precipitation occurs with calcium, strontium, barium, and magnesium. With copper the reagent forms a salt having the composition, $[C_6H_3BrNH_2CO_2]_2Cu$, and precipitates of a similar composition are obtained with cobalt, nickel and zinc. These complexes are similar to those formed with anthranilic acid.

5-Bromo-2-aminobenzoic acid has the advantage over anthranilic acid as a precipitant for metals, since the bromoanthranilates have a lower factor than the corresponding anthranilates. The metal bromoanthranilates are somewhat soluble in acetates and tartrates, but this difficulty is overcome by the use of an excess of the reagent.

The reagent is particularly useful for the determination of cobalt in the absence of heavy metals, since it is possible to weigh the complex directly. This is in contrast to many other cobalt reagents with which it is necessary to convert the complex to the oxide or sulfate before weighing. The following procedures for copper, cobalt, nickel and zinc have been proposed by Shennan.[3]

Reagent. Neutralize 5 g. of 5-bromo-2-aminobenzoic acid with a sodium hydroxide solution and dilute with distilled water to 500 ml.

Procedure. (*a*) *Determination of copper:* Dilute the solution to be analyzed to 100 ml., add a few drops of 5 N acetic acid and heat the mixture. Add 50 ml. of the reagent solution for each 0.05 g. of copper and heat gently for 30 minutes. Filter the light green precipitate through a No. 4 sintered glass crucible. Wash with hot water, dry at 105-110° C. for 1 hour and weigh. The copper factor is 0.1288. This procedure gives values which are correct to within 0.2 per cent of the true value.

(*b*) *Determination of cobalt:* The procedure for determining cobalt is exactly the same as that described for copper. The cobalt factor is 0.1206. Values correct to within 0.25 per cent are obtained by this method.

(*c*) *Determination of nickel:* In general the procedure for determining nickel is the same as that described for copper, but since the nickel salt is sparingly soluble in hot water, a different washing procedure must be employed. Use hot water containing 10 per cent of the precipitating reagent; this corresponds to 0.1 per cent 5-bromo-2-aminobenzoic acid, in which the nickel salt is insoluble. Finally, wash with a little cold water. The factor is 0.1200. An accuracy of 0.25 per cent is claimed.

(*d*) *Determination of zinc:* The procedure for zinc is the same as that for nickel. The factor is 0.1319 and the accuracy is 0.2 per cent.

Low values are obtained in the presence of sodium acetate, but this interference is eliminated by using a three-fold excess of the reagent.

1. A. S. Wheeler, *J. Am. Chem. Soc.* **31**, 565 (1909).
2. A. S. Wheeler and W. M. Oates, *J. Am. Chem. Soc.* **32**, 771 (1910).
3. R. J. Shennan, *J. Soc. Chem. Ind.* **61**, 164 (1942); *C.A.* **37**, 1095 (1943).

DIPHENYLENEGLYCINE

$C_{14}H_{11}O_2N$ Mol. Wt. 225.23 Beil. Ref. XX, 166

$$C_{12}H_8{=}N{-}CH_2{-}CO_2H$$

Use: Detection of nitrate.

Diphenyleneglycine is obtained as colorless glistening leaves from ethyl acetate. It melts at 215° C. It is soluble in ether, glacial acetic acid, alcohol, chloroform and xylene.

Preparation: Diphenyleneglycine is prepared by condensing completely dry potassium carbazol with chloroethylacetate at the boiling temperature, and saponifying the resulting carbazyl-N-acetic acid ester by heating with 35 per cent sodium hydroxide.[1,2]

Detection of nitrate. A sulfuric acid solution of diphenyleneglycine is recommended for the detection of small quantities of nitrates. This reaction is particularly useful when nitrite is present and when considerable quantities of halide are absent. The reagent is especially suited for the detection of solid nitrates. The color of the sulfuric acid solution of the reagent is a weak blue-green, but upon the addition of a little nitrate this turns to an intense yellowish-green. The test is carried out as follows:[3]

Procedure. Place 1 ml. of the solution to be tested in a test tube and add 5 ml. of concentrated sulfuric acid. Cool to room temperature with running water, and add 10-12 drops of a pale greenish-colored, 0.1 per cent solution of diphenyleneglycine in concentrated sulfuric acid. Shake well and observe the color. The sulfuric acid used in this test should previously be heated to 175° C. for one hour and then cooled. A freshly prepared solution of the reagent should be used. In case of doubt as to the color change, compare the test solution with a blank against a white background. By means of this reaction, nitrate can be detected at a concentration of 10 mg. of nitrate per liter of solution. Halides should be present only in traces.

1. *Chem. Z.* I, 350 (1913).
2. *Friedlander.* 11, 171.
3. M. Eitel, *Z. anal. Chem.* **98**, 227-34 (1934); *C.A.* **29**, 71 (1935).

GLYCINE

Synonym: Glycocol, aminoacetic acid

$C_2H_5O_2N$ Mol. Wt. 75.07 Beil. Ref. IV, 333

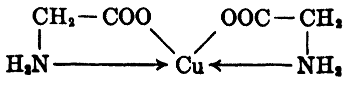
$$H_2N—CH_2—CO_2H$$

Use: Detection of copper and gold.

Glycine consists of colorless or white crystals. It melts at about 232-236° C. with decomposition. The compound is soluble in water, but is only slightly soluble in alcohol. It is insoluble in absolute alcohol and ether.

Preparation: Dissolve 104 g. of chloroacetic acid in 104 ml. of water, and run this solution slowly into 1,248 ml. of 28 per cent aqueous ammonia with stirring. When all the acid has been added, allow the mixture to stand 24 hours. Boil until all ammonia is expelled, and neutralize while hot with a slight excess of copper carbonate. Filter and evaporate the filtrate until crystallization begins. This point is determined by removing a small portion of the liquid and cooling on a watch glass. Filter the blue copper salt and wash, first with dilute, and then with absolute alcohol. Additional crystals are obtained by further evaporation. Dissolve the copper salt in water and precipitate while hot with hydrogen sulfide. Filter, wash, and evaporate the filtrate to a small volume on a water-bath. Crystals of glycine separate and are recovered.[1,2]

Detection of copper. A blue-colored copper complex having the formula



is formed when a solution of copper sulfate is added to glycine.[3-6]

Detection of gold. A violet color is obtained when a solution of glycine is added to a dilute solution of gold chloride. The test is best carried out by adding 1 ml. of a 0.1 per cent solution of glycine to 10 ml. of a solution containing about 0.002 per cent gold chloride.[7]

1. Perkin and Duppa, *Trans. Chem. Soc.* 11, 22 (1859).
2. K. Kraut, *Ann.* **266**, 292 (1891).
3. O. Schmitz-Dumont, *Metallwirtschaft.* 7, 281-5 (1929).
4. J. V. Dubsky, *Mikrochemie.* **23**, 42-50 (1937).
5. G. Bruni, *Zeit. Elektrochem.* 11, 93-4 (1905).
6. H. Ley, *Zeit. Elektrochem.* **10**, 954-6 (1904).
7. J. E. Saul, *Analyst.* **38**, 54 (1913).

5-NITROQUINALDINIC ACID

$C_{10}H_6O_4N_2$ Mol. Wt. 218.15 Beil. Ref. XXII, 73

$$O_2N—C_9H_5N—CO_2H$$

Use: Determination of zinc.

5-Nitroquinaldinic acid is a yellow solid which melts at 275-278° C. with decomposition. It is only slightly soluble in water and most organic liquids, but dissolves readily in acetic acid.

Preparation: Mix 4 g. of quinaldinic acid with a mixture of 5.6 ml. of concentrated sulfuric acid and 6.4 ml. of fuming nitric acid, and warm for 2 hours at 60-70° C. Pour the yellow solution into a large excess of water, whereupon the nitro compound separates as a yellow-white precipitate. Add sodium carbonate until the solution is clear, and precipitate while hot with pure sulfuric acid. Cool, filter with suction, and crystallize from water. This product consists of a mixture of 5- and 8-nitroquinaldinic acid. To separate the isomers, boil about 4 g. of the above product for a time with an excess of barium carbonate and a considerable quantity of water. Filter and allow the filtrate to cool. The barium salt of 5-nitroquinaldinic acid separates as fine needles. The free acid is obtained by decomposing the barium salt with dilute sulfuric acid and purifying by recrystallizing several times from water.[1]

Determination of zinc. Lott[2] has suggested the use of 5-nitroquinaldinic acid for the colorimetric microdetermination of zinc. Zinc is completely precipitated by the reagent from solutions of pH 2.5-8.0. The color of the reagent is not of sufficient intensity to be used for colorimetric measurement, but when treated with stannous chloride, a water-soluble, orange reduction product is formed which is suitable for a colorimetric comparison.

Reagents. *5-Nitroquinaldinic acid:* Crystallize a few g. of 5-nitroquinaldinic acid from water, and dry at 105° C. Dissolve 0.75 of the dried product in 100 ml. of warm 95 per cent ethyl alcohol. One ml. of this solution is equivalent to approximately 1 mg. of zinc.

Stannous chloride solution. Dilute 12.5 g. of $SnCl_2 \cdot 2H_2O$ in 100 ml. of hydrochloric acid ($d = 1.21$) and dilute to 500 ml. with water. Preserve over tin.

Procedure. Free the solution to be analyzed from interfering substances by the method of Boggs and Alben,[3] and pipet an aliquot containing 0.05-1.00 mg. of zinc into a 30-ml. beaker. Make the volume 5-10 ml. by dilution or evaporation, whichever is necessary, and add a drop of a 0.1 per cent alcoholic solution of methyl red. Make the solution just alkaline with 3 N ammonium hydroxide, and add acetic acid until the solution is distinctly acid (1-2 drops). Heat almost to boiling, and add a slight excess of the reagent solution. Allow the mixture to stand on a hot plate for 30 minutes without boiling and filter through an asbestos filter stick. Wash the beaker and the filter 5 times with boiling water, and dissolve the precipitate in 5 ml. of hot stannous chloride solution, and then heat to boiling. Filter off any asbestos, cool to room temperature, and compare in a colorimeter with standards containing known quantities of zinc and which have been similarly prepared. The standards and the unknown must be compared at the same temperature. When a photoelectric colorimeter is used, it is convenient to employ a graph prepared from readings made upon standard solutions.

Ammonium chloride and sodium chloride in concentrations greater than 0.7 N inhibit the complete precipitation of zinc.

The results obtained by using this method are shown in Table 26.

TABLE 26.—DETERMINATION OF ZINC WITH 5-NITROQUINALDINIC ACID

Zinc Used mg.	Zinc Found mg.
0.20	0.200
0.20	0.198
0.20	0.200
0.20	0.197
0.20	0.200
0.20	0.199
0.50	0.501
0.50	0.502
0.50	0.502
0.50	0.499

Silver, lead, mercury, copper, iron, manganese, cobalt and nickel form insoluble compounds with 5-nitroquinaldinic acid in slightly acid solutions and consequently must be removed before precipitating zinc with this reagent.

The color produced by treating the reagent with stannous chloride is stable for 24 hours. The intensity of this color is independent of acid concentration below 0.8 N, and of the concentration of stannous chloride over the range from 0.075 to 0.4 per cent of $SnCl_2 \cdot 2H_2O$. A rise in temperature increases the color intensity, and for this reason comparison of the unknown with the standard must be made at the same temperature.

1. E. Besthorn and S. Ibele, *Ber.* **39**, 2333 (1906).
2. W. L. Lott, *Ind. Eng. Chem., Anal. Ed.* **10**, 335-8 (1938); *C.A.* **32**, 6174 (1938).
3. H. M. Boggs and A. O. Alben, *Ind. Eng. Chem., Anal. Ed.* **8**, 97 (1936).

dl-PHENYLALANINE

Synonym: α-Amino-β-phenylpropionic acid

$C_9H_{11}O_2N$ Mol. Wt. 165.19 Beil. Ref. XIV, 498

$$C_6H_5—CH_2—CH(NH_2)—CO_2H$$

Use: Detection of cerium.

dl-Phenylalanine is obtained as crystalline leaves from aqueous alcohol. It melts at 271-273° C., and sublimes with partial decomposition. It is moderately insoluble in cold water, very slightly soluble in boiling alcohol, and is insoluble in ether.

Preparation: Dissolve 50 g. of benzylmalonic acid in 250 g. of dry ether, and add gradually in daylight 50 g. of bromine. Allow the mixture to stand 30 minutes after the addition of the bromine. Shake the ether solution with a little water, and gradually add sulfuric acid until the red color of bromine disappears. Separate the ether layer, wash with a little water, and carefully evaporate. Crystallize the solid residue from about 250 ml. of hot benzene.

Heat the benzylbromomalonic acid on an oil bath to 125-130° C. for 30-45 minutes. The residue is a yellow oil which does not crystallize, even at low temperature. This consists essentially of phenyl-α-bromopropionic acid. Wash with water, dissolve in ether, and dry over anhydrous sodium sulfate. Distill the ether and dissolve the oily residue in 5 times its volume of 25 per cent aqueous ammonia. Allow to stand 3-4 days at room temperature, or heat in a sealed tube for 3 hours at 100° C. Carefully evaporate the ammoniacal solution to dryness. Boil the residue with absolute alcohol to dissolve ammonium bromide, and recrystallize the residue of dl-phenylalanine from hot water.[5]

dl-Phenylalamine may also be prepared by heating phenylpyroracemic acid with concentrated ammonia under reflux to obtain the amide of phenacetylphenylalanine. This compound is hydrolyzed with dilute hydrochloric acid or sodium hydroxide to phenacetylphenylalanine, and this is converted to dl-phenylalanine by heating with concentrated hydrochloric acid in a tube at 250° C.[1-3]

Detection of cerium. *dl*-Phenylalanine reacts with solutions of ceric salts to yield a dark, blue-green precipitate. This is soluble in acids, and turns reddish-brown when treated with ammonium hydroxide. Solutions of thorium, titanium, zirconium, columbium, praseodymium and trivalent cerium salts do not give this test. This reaction is not sufficiently sensitive to be used as a spot test.[4]

1. E. Erlenmeyer, *Ber.* 30, 2927 (1897).
2. E. Erlenmeyer, *Ber.* 31, 2238 (1898).
3. J. Kunlin, *Ann.* 307, 154, 158 (1899).
4. F. M. Shemyakin and A. N. Belokon, *Compt. rend. acad. sci. (U.S.S.R.)* 18, 275-6 (1938); *C.A.* 32, 4470 (1938).
5. E. Fischer, *Ber.* 37, 3064 (1904).

PHENYLANTHRANILIC ACID

$C_{13}H_{11}O_2N$ Mol. Wt. 213.23 **Beil. Ref. XIV, 327**

$$C_6H_5—NH—C_6H_4—CO_2H$$

Use: Detection of vanadium.

Phenylanthranilic acid is a crystalline solid melting at 183-184° C.

Preparation: Mix 10 g. of *o*-chlorobenzoic acid, 10 g. of potassium carbonate, 40 mi. of aniline and 0.1 g. of precipitated copper in a round-bottomed flask. Fit the flask with a short vertical air condenser, and boil the mixture at such rate that a little water issues from the top of the condenser. Boil the mixture for 3 hours and remove the excess aniline by distillation with steam. Filter the residue while hot, boil the filtrate with animal charcoal and again filter. Acidify the hot filtrate with concentrated hydrochloric acid and allow to stand until cold Filter off the crystals of phenylanthranilic acid and wash with cold water and dry. Purify by recrystallizing from acetic acid and alcohol.[1,2]

Detection of vanadium. Phenylanthranilic acid may be used in a sensitive reaction for the detection of vanadium in steel.[3]

Procedure. Dissolve the steel in several drops of 1:1 sulfuric acid and transfer the resulting solution to a microcrucible. Decompose carbides by heating with hydrogen peroxide and add 0.5 N potassium permanganate. Reduce the excess permanganate with 0.5 N sodium nitrite and decompose the excess nitrite with urea. Add 0.5 ml. of 1:1 sulfuric acid and a little phenylanthranilic acid. A red-violet color is obtained with vanadium. This reaction is sensitive but requires considerable care.

The above test may be carried out by applying sulfuric acid to the surface of the steel to be tested without destroying the sample.

1. C. Graebe and K. Lagodzinski, *Ber.* 25, 1734 (1892).
2. F. Ullmann, *Ber.* 36, 2382 (1907).
3. L. P. Adamovich and A. Zagorul'ko, *Zavodskaya Lab.* 9, 465-6 (1940); *C.A.* 37, 1346 (1943).

PICOLINIC ACID

Synonym: 2-Pyridinecarboxylic acid

$C_6H_5O_2N$ Mol. Wt. 123.10 Beil. Ref. XXII, 33(402)

$C_5H_4N—CO_2H$

Use: Reaction for silver.

Picolinic acid, an isomer of nicotinic acid, is a white to slightly reddish crystalline powder. It melts at 136-137° C. It is sparingly soluble in cold water, soluble in hot water or alcohol, but is insoluble in benzene, chloroform, and carbon disulfide.

Preparation: Mix 20 g. of α-picoline with 36 g. of potassium permanganate in 900 ml. of water and heat on a water bath. Add an additional 36 g. of potassium permanganate dissolved in 400 ml. of water as the color is destroyed. Filter off the hydrated oxide of manganese and wash well. Distill off 200 ml. of the filtrate, and almost neutralize the remainder with dilute sulfuric acid. Evaporate until crystals begin to form and allow to cool. Filter off the potassium sulfate, wash well with aqueous alcohol, and make the combined filtrate and washings slightly acid. Precipitate the picolinic acid by adding an excess of a hot, saturated solution of copper sulfate. Filter off the copper salt, wash thoroughly, and suspend it in 150 ml. of boiling water. Treat with hydrogen sulfide to decompose the salt, and then filter. Evaporate the filtrate to dryness, and purify by recrystallizing from water or alcohol containing a little decolorizing charcoal.[1,3]

Reaction with silver. Silver picolinate ($Ag(C_5H_4NCO_2)_2$) is prepared by adding a solution containing 1.7 g. of silver nitrate dissolved in 50 ml. of water to 3.7 g. of picolinic acid dissolved in 50 ml. of water. Dissolve the precipitate which forms in 2.5 g. of sodium carbonate and treat with 2.0 g. of potassium persulfate dissolved in 60 ml. of water. The original red needles which separate are only slightly soluble in water, but dissolve in hydrochloric acid with evolution of chlorine and reprecipitation of silver chloride. The compound is thought to be an inner-complex salt in which silver is coordinated to the nitrogen atom. This reaction is of doubtful analytical value.[2]

1. H. Weidel, *Ber.* 12, 1992 (1879).
2. G. A. Barbieri, *Atti accad. Lincei.* 17, 1078-81 (1933); *C.A.* 28, 2291 (1934).
3. G. R. Clemo and G. R. Ramage, *J. Chem. Soc.* 134, 440 (1931).

QUINALDINIC ACID

Synonym: Quinoline-2-carboxylic acid, quinaldic acid

$C_{10}H_7O_2N \cdot 2H_2O$ Mol. Wt. 209.20 Beil. Ref. XXII, 71

$C_9H_6N—CO_2H$

Use: Detection of copper.

Determination of cadmium, copper, iron, uranium and zinc.

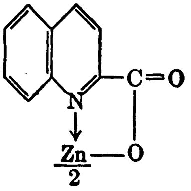
Quinaldinic acid occurs as white, odorless crystals or as a crystalline powder. It melts at 155-157° C. (anhydrous). It is moderately soluble in water, soluble in alcohol and alkali solutions.

Preparation: *Tribromoquinaldine:* Mix 50 g. of dry, powdered sodium acetate, 100 g. of glacial acetic acid, and 14 g. of pure quinaldine, and heat to 70° C. To the hot solution, add during a period of 10 minutes, and with thorough shaking, a solution containing 48 g. of bromine dissolved in 100 g. of glacial acetic acid. Boil for a few minutes, allow to stand 30 minutes on a water bath, and then let the mixture cool to room temperature. Pour the mixture into water and separate the precipitate by filtration. Wash the product and dry, and then recrystallize from alcohol or glacial acetic acid.

Some samples of quinaldine yield a tarry material when the reaction mixture is poured into water, and this is difficult to remove. A good product is obtained by allowing the acetic acid solution to cool, and omitting the treatment with water. A mixture of sodium bromide and tribromoquinaldine separates under these conditions. Filter this mixture, wash with cold glacial acetic acid, and finally with water.

Quinaldinic acid: Mix the tribromoquinaldine with 1:10 sulfuric acid, and boil under reflux until a test portion on neutralization yields no unchanged bromine compound. Cool, nearly neutralize, and add an excess of a copper sulfate solution. Filter off the insoluble copper salt, wash, suspend in hot water, and then precipitate all copper with hydrogen sulfide. Filter off the copper sulfide. Evaporate the filtrate to dryness, and recrystallize from glacial acetic acid.[1,17]

Reactions of quinaldinic acid. Quinaldinic acid reacts with a number of metallic ions to form chelate compounds of the type indicated by the probable formula of the zinc complex



Such reactions have been used for the colorimetric determination of iron, and for the quantitative precipitation of copper, cadmium, uranium, and zinc. Cadmium forms an insoluble precipitate in neutral solutions; cadmium, copper, ferrous iron and zinc in acid solutions; uranium in an ammonium chloride solution; and zinc in dilute acetic acid.

Detection and determination of copper. The sodium salt of quinaldinic acid may be used for the detection and determination of copper. In the absence of iron and zinc, copper may be detected with the aid of this reagent. Since copper quinalidinate is insoluble in dilute sulfuric acid and in dilute acetic acid, the determination of copper may be carried out in either of these media with little interference except from zinc and iron.

Reagent. Dissolve 5.636 g. of sodium quinaldinate, corresponding to 5 g. of quinaldinic acid, in 150 ml. of water.

Procedure. Add 2-5 ml. of 2 N sulfuric acid to a solution containing 10-50 mg. of copper in a volume of 150 ml. Heat to boiling, and add dropwise the 3.5 per cent sodium quinaldinate solution until precipitation is complete. Allow to stand for a few minutes, and filter the light green precipitate through a filter crucible. Wash the precipitate by decantation with hot water, transfer to the filter crucible, and again wash with hot water until all traces of the reagent are removed. Dry at 125° C. and weigh as $Cu(C_{10}H_6NO_2)_2 \cdot H_2O$. The factor for copper is 0.1496.

Excellent results are claimed for this method.

Kiba and Sato[11] recommend a temperature of 110-140° C. as suitable for drying the precipitate of copper quinaldinate.

Zan'ko and Butenko[4,5] have proposed a method for determining copper in cast iron and steel. The method is based on the relative instability of the copper tartrate complex at a definite acidity of solution, and on the fact that copper quinaldinate is less soluble than the corresponding quinaldinates of the other elements contained in steel and cast iron. The method gives results accurate within 0.02 per cent of the weight of the sample.

Procedure. Dissolve 1 g. of the material in 15-20 ml. of 1:1 hydrochloric acid, add 2-3 ml. of concentrated nitric acid, and boil until the oxides of nitrogen are completely expelled. Transfer the solution to a porcelain dish and evaporate to dryness. Filter any undissolved silica, ignite, and then treat with hydrofluoric and sulfuric acids to remove silica. Dissolve the residue in water and add to the original filtrate.

Add 6 g. of tartaric acid and neutralize with ammonium hydroxide, and then add 15 ml. of 4 N sulfuric acid. Now precipitate copper by the dropwise addition of sodium quinaldinate. Let stand 18 hours, filter through a filter crucible, wash with hot water, dry at 125° C. and weigh. The factor for copper is 0.1496.

A method for the microdetermination af approximately 1 mg. of copper has been described by Ray and Rose.[9]

Separation of copper. Quinaldinic acid has been used to separate copper from cadmium, lead, manganese, nickel, cobalt, and arsenic and phosphoric acids.[2,3] The conditions necessary for these separations are described in the following paragraphs:

(a) *Separation of copper and cadmium.* Copper is precipitated exactly as described in the determination of copper. To determine cadmium, the filtrate and wash liquid from the copper precipitation are evaporated to 160 ml., and neutralized with ammonium hydroxide. Cadmium is completely precipitated on the addition of more sodium quinaldinate.

Shennan[12] claims that the method of Ray and Bose[2] is excellent for determining either copper or cadmium when only one of these elements is present, but according to his investigations the separation of copper and cadmium is unsatisfactory. On the other hand, Majundar [13] states that copper and cadmium are separated satisfactorily by means of quinaldinic acid if the acidity of the solution is adjusted to pH 1.22-2.01. Lindsey and Shennan,[14] however, point out that for the complete precipitation of copper from solutions containing 10 ml. of 2 N sulfuric acid, a three-fold excess of reagent is necessary. When the procedure is applied to the separation of copper and cadmium, results show that the copper values are high and cadmium values are low.

In a series of investigations, Majundar [16] found that results obtained in separating 26-53 mg. of copper and 31-92 mg. of cadmium are excellent. He further states that the solubility of copper quinaldinate in acetic acid is a specific effect and not one of pH. Thus, 13.4 mg. of the copper salt dissolves in acetic acid of pH 2.05, while in the same volume of sulfuric acid of pH 2.05 only 1.3 mg. dissolves.

(b) *Separation of copper from lead.* The following method is used for the separation of copper and lead:

Procedure. Add 7-15 ml. of glacial acetic acid to the unknown solution and dilute to 200 ml. Heat to boiling and add dropwise to the hot solution a 3.5 per cent solution of sodium quinaldinate until precipitation is complete, and then add an additional 1 ml. Filter through a filter crucible, and wash the precipitate with a solution containing 1 ml. of glacial acetic acid and 3-5 drops of sodium quinaldinate in 50 ml. of water. Finally wash the precipitate several times with hot water and dry at 125° C. to constant weight.

Lead is determined in the filtrate according to one of the standard methods, preferably as the sulfate by heating with sulfuric acid.

(c) *Separation of copper from manganese, cobalt and nickel.* To precipitate copper in the presence of manganese, cobalt and nickel, add 5-8 ml. of 2 N sulfuric acid to the unknown solution and dilute to 200 ml., and precipitate copper with sodium quinaldinate as described above. As wash solution, use hot water containing 2.5 ml. of 2 N sulfuric acid and 1 ml. of 3.5 per cent sodium quinaldinate solution per 100 ml. The precipitate is finally washed several times with hot water to remove the last traces of the sodium salt.

(d) *Determination of copper in the presence of phosphoric acid, arsenic acid or arsenious acid.* To precipitate copper in the presence of phosphoric acid, arsenic acid or arsenious acid, the acidity should correspond to 6-10 ml. glacial acetic acid in a total volume of 200 ml. The wash solution is prepared by adding several drops of 3.5 per cent sodium quinaldinate solution to 1:40 acetic acid.

Determination of cadmium. The cadmium salt of quinaldinic acid is quantitatively precipitated from a neutral solution or from a solution made acid with acetic acid. On drying at 125° C. the cadmium salt is anhydrous, and corresponds to the formula, $Cd(C_{10}H_6NO_2)_2$. The formation of this compound has been made the basis of a method for determining cadmium.[2]

Procedure. Adjust the volume of the solution to 150 ml. for 0.1-0.2 g. of cadmium, and warm on a water bath for several minutes. Add dropwise and with constant stirring a 3.5 per cent solution of sodium quinaldinate until precipitation is complete. Carefully add dilute sodium hydroxide until the mixture is just neutralized, and allow the white, granular precipitate to settle. Cool to room temperature, wash the precipitate by decantation with cold water, and transfer to a filter crucible. Wash with cold water until the precipitate is free of excess reagent. Dry to constant weight at 125° C. and weigh. The factor for cadmium is 0.2462.

Kiba and Sato[11] recommend a temperature of 110-125° C. as suitable for drying the precipitate of cadmium quinaldinate.

Determination of uranium. Uranium forms basic salts with quinaldinic acid. The composition of the precipitate has not been determined, but uranium is completely precipitated in this manner.[2]

Procedure. Add 5-7 g. of ammonium chloride to a solution of uranyl nitrate, dilute to 120 ml., and heat to boiling. Add dropwise and with stirring a 3.5 per cent solution of sodium quinaldinate to the hot uranium solution until precipitation is complete. Transfer the precipitate to a filter, and wash with a hot solution containing 5 per cent hexamethylenetetramine and 5 per cent ammonium nitrate until the washings are free of chloride. Place the wet precipitate in a platinum crucible, and ignite and weigh as U_3O_8.

Determination of zinc. Zinc is quantitatively precipitated from acetic acid solutions with quinaldinic acid. This reaction has been used for the quantitative determination of zinc.[2]

Procedure. To 150 ml. of solution containing 0.1 g. of zinc, add 2-5 ml. of dilute acetic acid and heat to boiling. Add dropwise and with stirring a 3.5 per cent solution of sodium quinaldinate until precipitation is complete. Wash the precipitate by decantation with hot water, transfer to a filter crucible, and again wash with hot water until all traces of reagent are removed. Dry at 125° C. to constant weight. The factor for zinc is 0.15295.

A temperature range of 110-170° C. is suitable for drying the precipitate of zinc quinaldinate.[11]

Separation of zinc. In an acid solution, sodium quinaldinate causes a partial precipitation of the basic salts of iron, aluminum, chromium, beryllium, titanium, and uranyl ions, but the precipitation of these ions does not take place in the presence of an alkali tartrate. Since zinc is quantitatively precipitated from solutions containing acetic acid and alkali tartrates with sodium quinaldinate, this reagent provides an excellent method for determining zinc in the presence of the above metals. The zinc salt is soluble in excess ammonium hydroxide and alkalies. The presence of chromium is reported to interfere somewhat with this determination.[6,10]

Procedure. To a cold solution containing zinc and other ions, with iron in the ferric state, add 4-5 g. of Rochelle salt and some ammonium chloride.

Neutralize with dilute ammonium hydroxide, using a mixture of methyl red and methylene blue as indicator. Add 1-2 drops of 2 N ammonium hydroxide in excess, dilute to 150 ml. and heat to 50° C. Add dropwise, with stirring, a slight excess of ammonium quinaldinate. Filter, and wash the precipitate with hot water. Dry at 125° C. and weigh as $Zn(C_{10}H_6NO_2)_2 \cdot H_2O$. The factor for zinc is 0.1529.

Ordinarily the presence of copper, silver, and mercury interferes, since these ions form less soluble quinaldinates than that of zinc. It is impossible to separate the zinc by dissolving zinc quinaldinate with dilute mineral acids, since some of this salt is firmly retained by the other precipitates. The addition of thiourea to the solution containing the zinc salt causes the formation of complexes with interfering ions, and these complexes do not react with quinaldinic acid. Cupric ions, however, must first be reduced to the cuprous state by treatment with sodium bisulfite.[7,8]

Procedure. Neutralize the solution containing zinc and copper, and add 2-5 ml. of dilute acetic acid. Then add a freshly prepared solution containing 4-8 g. of sodium bisulfite, depending upon the copper content, and finally a solution of 4-8 g. of thiourea, also depending on the copper content. Dilute the mixture to 200 ml., and heat, and to the hot solution add dropwise an excess of a neutral 5 per cent solution of sodium quinaldinate. Allow the precipitate to settle while heating on a hot water bath. Wash the precipitate thoroughly by decanting with hot water, and continue the washing until a portion of the filtrate gives no test for excess reagent with ferrous sulfate. Dry at 125° C. and weigh as $Zn(C_{10}H_6NO_2)_2 \cdot H_2O$. The factor for zinc is 0.1529.

Results with samples containing 15-50 mg. of zinc are excellent.

A similar method is used for the determination of zinc in the presence of mercury and silver, except that the sodium bisulfite is not used, and the solution is diluted to a volume of 300 ml. before precipitating zinc with sodium quinaldinate.

It is also possible to determine zinc in the presence of iron, aluminum, uranium, beryllium and titanium by means of a micromethod.[9,10]

Procedure. Dissolve the sample containing 0.15-1.0 mg. of zinc in about 1.5 ml. of water. If iron is present, add a few drops of bromine water to oxidize it to the ferric state, and then add 0.4-1.0 ml. of a 5 per cent sodium tartrate solution. Blow ammonia vapor over the surface of the solution until a sufficient quantity has dissolved to impart an odor to the solution. Now precipitate zinc by the dropwise addition of a 1 per cent solution of sodium quinaldinate, and then add 0.2-0.25 ml. of the reagent in excess. Gently warm the beaker on a water bath to 60° C., and remove the ammonia by blowing air through a capillary over the surface of the liquid. Be sure that the temperature does not exceed 60° C. Cool rapidly, and filter at once through an Emich asbestos-packed filterstick. Wash the precipitate with hot water and dry in a current of air at 125° C. The factor for zinc is 0.1529.

The accuracy of this method in the presence of iron and aluminum is shown in Table 27.

TABLE 27.—DETERMINATION OF ZINC IN THE PRESENCE OF IRON AND ALUMINUM

	Metal Added	Na Tartrate Solution	ml. of Reagent	Zn Found	Zn Added
1.	2.5 mg. Fe	0.5 ml.	0.7	0.5581	0.5551
2.	2.5 mg. Fe	0.5 ml.	0.9	1.0750	1.0690
3.	2.0 mg. Fe	0.4 ml.	0.8	0.8680	0.8728
4.	3.0 mg. Fe	0.6 ml.	0.5	0.3309	0.3308
5.	4.0 mg. Fe	0.8 ml.	0.5	0.3784	0.3774
6.	5.0 mg. Fe	1.0 ml.	0.45	0.3764	0.3775
7.	5.0 mg. Fe	1.0 ml.	0.4	0.1888	0.1894
8.	6.0 mg. Fe	1.2 ml.	0.35	0.1245	0.1237
9.	5.5 mg. Al	1.0 ml.	0.5	0.2765	0.2765
10.	6.0 mg. Al	1.0 ml.	0.4	0.1900	0.1897
11.	5.5 mg. Al	1.0 ml.	0.6	0.6039	0.6042

Recent studies by Shennan[12] indicate that quinaldinic acid offers a convenient, rapid, and accurate method for determining copper, cadmium, or zinc alone, but it seems that this method is unsuited for the separation of these metals.

A number of special separations have been reported:

(a) *Separation of zinc from manganese.* This separation is based on the solubility of manganese quinaldinate in dilute acetic acid.[2,6,9]

Procedure. Add 5-10 ml. of glacial acetic acid for each 200 ml. of the sample solution, and heat to boiling. Add dropwise and with stirring a 3.5 per cent solution of sodium quinaldinate until precipitation is complete. Decant the mixture through a filter crucible, transfer the precipitate to the crucible with hot, 1:40 acetic acid, and wash with hot water.

Manganese in the filtrate may be precipitated as the sulfide and determined as manganese sulfate.

(b) *Separation of zinc from magnesium.* Zinc is separated from magnesium by the following procedure:[6]

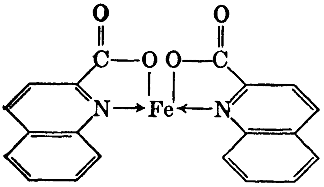
Procedure. Dilute the unknown solution to about 200 ml., and add 2 ml. of glacial acetic acid. Precipitate zinc by adding a 3.5 per cent solution of sodium quinaldinate dropwise and with stirring. Allow to stand for a time and filter through a filter crucible. Wash the precipitate with hot water, and in the filtrate determine magnesium as the pyrophosphate.

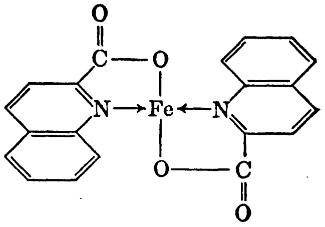
(c) *Separation of zinc from calcium and barium.* Zinc is separated from calcium and barium in about the same manner as from magnesium.[6] Zinc is precipitated from a solution containing 3-6 ml. of glacial acetic acid in a total volume of 170 ml.

(d) *Separation of zinc from phosphoric acid.* Zinc is separated from phosphoric acid by the following procedure:

Procedure. Add sodium carbonate to the solution containing zinc and phosphoric acid until a turbidity appears, and then clarify by adding 6 ml. of glacial acetic acid. Dilute with water to a volume of 200 ml. and heat. The solution should remain clear during the heating period. Precipitate zinc by adding a 3.5 per cent solution of sodium quinaldinate dropwise to the hot solution until precipitation is complete. Filter and wash with water containing several drops of acetic acid and the reagent solution, and finally wash with pure water.

Determination of iron. Sodium quinaldinate reacts with cold, neutral solutions of ferrous iron to form a dark red, fairly soluble precipitate; but this precipitate changes, particularly with rising temperature, to a less soluble, bluish-violet modification. This change appears to be due to the existence of *cis-* and *trans-* isomers of the ferrous complex.[2]





The color reaction between ferrous iron and sodium quinaldinate has been used for the detection and colorimetric determination of iron.[2,15] The intensity of the color reaction is enhanced by the addition of a dilute solution of potassium cyanide. Hydroxylamine hydrochloride is used to reduce ferric iron to the ferrous condition. This reaction is sensitive to 0.172γ of iron at a concentration limit of 1:14,500,000.

Procedure. If phosphoric acid is absent, proceed as follows: Free sample of silicic acid in the usual manner, and, if the quantity of aluminum present is less than 4-5 per cent, make up in a volumetric flask, and transfer an aliquot to a 100-ml. volumetric flask. Dilute the aliquot to 70-75 ml. and neutralize with ammonium hydroxide to an end-point with methyl yellow. Treat the resulting solution with 1 ml. of 5 per cent hydroxylamine hydrochloride, then add 1 ml. of 1 per cent sodium quinaldinate solution, and finally add 1 ml. of 10 per cent potassium cyanide and dilute to the mark. Filter, and compare the resulting solution with a standard in a colorimeter.

In the presence of more than 4-5 per cent of aluminum, it is necessary to precipitate all the trivalent hydroxides with ammonium hydroxide, then dissolve the precipitate in hydrochloric acid and proceed as above.

In the presence of phosphoric acid, proceed as above but add to the standard solution the same quantity of phosphoric acid as contained in the sample.

During the color comparison, both sample and standard must be cooled to retard the fading of the pale red color.

By this method iron may be determined in the presence of moderately large amounts of copper, nickel, cobalt and zinc.

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QUINOLINE-8-CARBOXYLIC ACID

$C_{10}H_7O_2N$ Mol. Wt. 173.16 Beil. Ref. XXII, 81

$C_9H_6N—CO_2H$

Use: Detection of cadmium, copper, iron, lead, mercury, silver and thallium.

Determination of copper.

The compound is obtained as needles by crystallizing from water. The melting point is 186-187.5° C. It sublimes above its melting point. The reagent is markedly soluble in cold water, moderately soluble in hot water and in alcohol, and very soluble in acids and alkalies.

Preparation: Mix 9 g. of *o*-nitrobenzoic acid, 15 g. of *o*-aminobenzoic acid, 20 g. of glycerol and 25 g. of sulfuric acid, and heat for 3 hours in a flask fitted with a reflux condenser. Heat on a sand bath at a temperature of 140-145° C. Dissolve the reaction product in water, and add sufficient barium chloride to precipitate barium sulfate. Filter, and evaporate the filtrate on a water bath to a thin syrup. Allow to stand overnight. Fine needles of quinoline-8-carboxylic acid hydrochloride separate. Add alcohol to complete the separation. Recrystallize from dilute alcohol containing a little hydrochloric acid, and finally crystallize from a solution containing a little decolorizing charcoal.

More of the hydrochloride may be obtained from the mother liquor by diluting with water, nearly neutralizing with ammonia, and precipitating the warm solution with copper acetate. Suspend the well-washed precipitate in dilute hydrochloric acid and decompose with hydrogen sulfide. Filter and concentrate the filtrate.

To obtain the free acid, treat one half of the aqueous solution with ammonia to the complete disappearance of the needles, and then combine with the other half. The mass solidifies to a paste, which is purified by repeated crystallization from water.[1]

Determination of copper. In neutral solutions, quinoline-8-carboxylic acid precipitates cadmium, lead, mercuric, thallous, copper and silver salts. Ferrous salts give a red coloration. All of these salts are soluble in strong mineral acids. Copper may be determined with good results by precipitating with quinoline-8-carboxylic acid, and then weighing the copper salt after drying. From 6-250 mg. of copper may be determined satisfactorily by the following method, which has been proposed by Majunder.[2]

Procedure. Dilute the solution to be analyzed to about 150 ml., neutralize if necessary with ammonia, and add 2-14 ml. of 0.1 N sulfuric acid. Add dropwise, at room temperature, a 1 per cent solution of the alkali salt of quinoline-8-carboxylic acid. Filter through a Gooch crucible and wash with hot water. Dry at 150° C. and weigh as $Cu(C_{10}H_6O_2N)_2$. The factor for copper is 0.1559.

For reasons not easily understood, the copper salt appears to be more soluble in acetic acid solutions than in sulfuric acid solutions of the same pH.

The following method is recommended by Gilbreath and Haendler:[3]

Procedure. To a solution containing about 50 mg. of copper per 100 ml. of solution, add a slight excess of ammonium hydroxide, and carefully add 3 N acetic acid until the blue color just disappears, and then add 3 drops in excess. Heat to boiling and add 60 ml. of a saturated aqueous solution of quinoline-8-carboxylic acid. About 0.4 g. of the solid reagent is required for each 50 mg. of copper. Stir for one minute, cool for 2 hours, filter, wash with a little 1 per cent solution of the reagent, and finally with a little water. Dry the precipitate at 110-120° C. and weigh. The precipitate contains 15.59 per cent copper.

This procedure can be used for separating copper from cadmium and zinc. Silver and gold interfere.

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1. A. Schlosser and Z. H. Skraup, *Monatsh.* **2**, 530 (1881).
2. A. K. Majundar, *J. Indian Chem. Soc.* **18**, 419-22 (1941) ; *C.A.* **36**, 3449 (1942).
3. J. R. Gilbreath and H. M. Haendler, *Ind. Eng. Chem., Anal. Ed.* 14, 866 (1942) ; *C.A.* **37**, 577 (1943).

CHAPTER V

MISCELLANEOUS ACIDS

ACETYLSALICYLIC ACID

Synonym: Aspirin

$C_9H_8O_4$ Mol. Wt. 180.15 Beil. Ref. X, 67

$CH_3—CO—O—C_6H_4—CO_2H$

Use: Detection of manganese.

Acetylsalicylic acid consists of white odorless crystals or a white crystalline powder. It is stable in dry air but is decomposed in the presence of moisture into salicylic and acetic acids. It melts at 135° C. when rapidly heated. One gram of the solid dissolves in 300 ml. of water, 5 ml. of alcohol, 17 ml. of chloroform and 10-15 ml. of ether.

Preparation: Mix 14 g. of salicylic acid and 10 g. of pyridine and cool the mixture in ice. Then add dropwise 10 g. of acetyl chloride with constant stirring. Heat the mixture on a water-bath for 2 minutes and cool. Add a small quantity of crushed ice and stir into the viscous semi-solid mass, whereupon crude acetylsalicylic acid solidifies. Filter, wash with water, and dry on a porous plate.[1]

Detection of manganese. When an ammoniacal solution of acetylsalicylic acid is added to a solution containing a manganese salt and the mixture is treated with hydrogen peroxide, a red to brown color is obtained. This reaction has been used by Fulton [2] as a sensitive test, both for acetylsalicylic acid and for manganese.

Reagent. Dissolve 0.3 g. of acetylsalicylic acid in 1 ml. of 10 per cent ammonium hydroxide and add 0.5 ml. of hydrogen peroxide.

Procedure. When the above reagent is added to a neutral solution containing manganese, a red to brown color appears. As little as 0.5γ of manganese in 5 ml. of solution can be detected by this method. The limit of dilution is 1:10,000,000. Ferric iron gives a similar reaction.

Wenger and co-workers,[3] who have conducted a critical survey of the reactions used for detecting manganese, recommend the use of acetylsalicylic acid.

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[1] J. Wohlgemuth, *Chem. Zentr.* I, 1294 (1899).

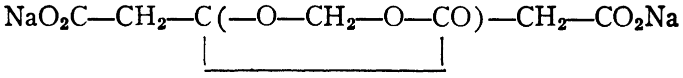
[2] C. C. Fulton, *Am. J. Pharm.* 105, 59 (1933).

[3] P. Wenger, R. Duckert, and M. L. Busset, *Helv. Chim. Acta.* 24, 1143-50 (1941); *C.A.* 36, 3450 (1942).

CITARIN

Synonym: Anhydromethylenecitraconic acid (sodium salt)

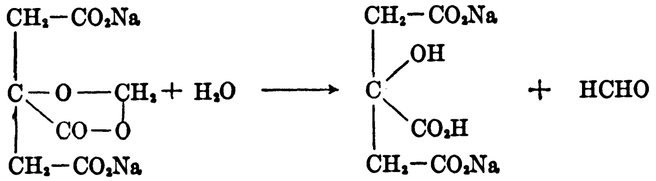
$C_7H_6O_7Na_2$ Mol. Wt. 248.12 Beil. Ref. XIX, 313(759)



$$NaO_2C—CH_2—C(—O—CH_2—O—CO)—CH_2—CO_2Na$$

Use: Determination of gold and silver.

The free acid is obtained as a crystalline compound from water. It melts at 208° C. It is soluble in 12 parts of cold water, but dissolves readily in hot water, acetone and chloroform. It is only slightly soluble in alcohol and is almost insoluble in ether. The sodium salt (citarin) is a colorless powder which dissolves readily in cold water. On warming with water the compound decomposes with the formation of formaldehyde according to the following equation:



Preparation: Citarin may be prepared by heating 200 g. of citric acid with 30 g. of paraformaldehyde to a temperature of 140-160° C. and extracting the free acid with water. The sodium salt is formed by neutralization.

The compound may also be prepared by evaporating 200 g. of citric acid with 150 g. of formalin and 150 g. of concentrated hydrochloric acid on a water-bath.[1]

Determination of gold and silver. Vanino and Guyot[2] recommend the use of citarin as a precipitant for gold and silver from solutions of the salts of these metals. The reagent acts indirectly as a reducing substance, due to the fact that formaldehyde is formed when the compound is heated with water, and the formaldehyde acts in the usual manner to reduce alkaline solutions of gold and silver salts to the free metal. When an aqueous solution of silver nitrate is heated for 30 minutes in the presence of sodium hydroxide and citarin, metallic silver is quantitatively precipitated according to the following reaction:

$$2AgNO_3 + C_7H_6O_7Na_2 + 3NaOH \rightarrow$$
$$2Ag + HCOONa + 2NaNO_3 + C_6H_6O_7Na_2 + H_2O$$

To determine silver, allow the mixture to stand overnight, filter through a Gooch crucible, wash, dry at 110-120° C. and weigh. The results of silver determinations using this method are shown in Table 28, taken from the work of Vanino and Guyot:

TABLE 28.

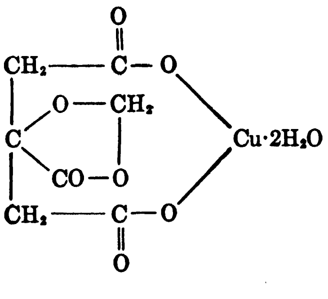
$N/10AgNO_3$ ml.	N/10NaOH ml.	N/10 Citarin ml.	Ag Used g.	Ag Found g.	Difference Per Cent
10	15	10	0.1078	0.1084	+0.55
10	15	10	0.1078	0.1076	—0.18
10	30	20	0.1078	0.1074	—0.37
10	30	20	0.1078	0.1084	+0.55
10	30	20	0.1078	0.1076	—0.18

Solutions of gold salts are reduced to metallic gold by means of citarin in an alkaline solution according to the following equation:

$$2AuCl_3 + 3NaOH + 3C_7H_6O_7Na_2 \rightarrow$$
$$2Au + 3HCO_2Na + 6NaCl + 3C_6H_6O_7Na_2 + 3H_2O$$

and the gold may be determined by weighing the metal in a manner similar to that employed with silver.

Reactions with the metals. Vanino and Guyot[3] have studied the reactions of concentrated aqueous solutions of citarin with solutions of salts of many of the metals. They have found that many of the metals react with citarin to form salts in which the 2 sodium atoms are replaced by the equivalent of other metals. The composition of the copper salt, which is typical of the metallic salts, is represented by the following formula:



Certain of the reactions of citarin with metallic salts are due to the reduction of the cation by the formaldehyde which is formed by the hydrolysis of the reagent. The reactions obtained with citarin and various metallic salts are listed in Table 29:

TABLE 29.

Salt	Reaction
Silver nitrate	White precipitate.
Copper sulfate	Green solution with excess of citarin. This is stable on boiling, but metallic copper is precipitated in the presence of sodium hydroxide.
Beryllium chloride	Immediate white precipitate, soon changing to transparent viscous mass.
Magnesium sulfate	Crystalline precipitate after a short time.
Calcium chloride	Fine crystalline precipitate on standing.
Strontium chloride	An amorphous precipitate gradually forms.
Cadmium sulfate	A crystalline precipitate gradually forms.
Mercurous nitrate	A white precipitate forms which is soluble in a large excess of citarin. A very small reduction occurs on boiling.
Mercuric nitrate	A white precipitate forms which is soluble in large excess of reagent. No reduction occurs when mixture is boiled.
Aluminum chloride	A heavy white precipitate forms.
Lead nitrate	A white amorphous precipitate forms.
Chrome alum	Immediate crystalline precipitate.
Uranyl acetate	No precipitation.
Manganous sulfate	Crystalline precipitate.
Ferric chloride	A red-brown precipitate forms which is soluble in excess of reagent. The compound is not precipitated with ammonia, but a red-brown color develops.
Ferrous ammonium sulfate	Gradual yellowish-white amorphous precipitate.
Bismuth nitrate	Immediate white amorphous precipitate.
Stannous chloride	Immediate white amorphous precipitate.

1. W. Sternberg, *Chem. Zentr.* **I**, 300 (1902).
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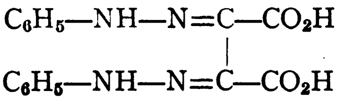
3. L. Vanino and O. Guyot, *Arch. Pharm.* **264**, 113-17 (1926); *C.A.* **20**, 1685 (1926).

DIHYDROXYTARTARIC ACID OSAZONE

$C_{16}H_{14}O_4N_4$ Mol. Wt. 426.27 Beil. Ref. XV, 383.



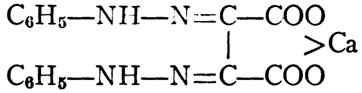
$$\begin{array}{l} C_6H_5-NH-N=C-CO_2H \\ \qquad\qquad\qquad\qquad\;\; | \\ C_6H_5-NH-N=C-CO_2H \end{array}$$

Use: Detection of calcium.

This compound is an orange-yellow powder. It is easily soluble in warm alcohol and acetic acid, but is only slightly soluble in water.

Preparation: Dissolve 30 g. of phenylhydrazine hydrochloride in 500 ml. of water and mix this solution with 20 g. of sodium dihydroxytartarate (for preparation, see page 108) in 80 ml. of 18 per cent hydrochloric acid. Heat the mixture for 30 minutes on a water-bath. Filter the precipitated osazone, wash well with alcohol, dry, and digest for a time in a flask with a little alcohol. Then add the calculated quantity of 10 per cent alcoholic sodium hydroxide to form the sodium salt of the compound. Filter, wash with alcohol, and dry.[1]

Detection of calcium. An aqueous solution of dihydroxytartaric acid osazone yields bright yellow flocculent precipitates when added to solutions of the alkaline earth salts.[2-5,7] The structure of the calcium salt is indicated in the following formula.



$$\begin{array}{l} C_6H_5\text{—NH—N}=\text{C—COO} \\ \qquad\qquad\qquad\quad | \qquad\quad >\text{Ca} \\ C_6H_5\text{—NH—N}=\text{C—COO} \end{array}$$

The calcium salt is quite insoluble in water, and its formation may be utilized in testing for calcium in solutions containing very low concentrations of that ion. Due to the fact that the reagent is not specific in its action, other metals, with the exception of alkali and ammonium salts, must be absent in making the test. Magnesium does not interfere unless it is present in quantities exceeding 10 times the amount of calcium. In higher concentrations of the magnesium ion, the magnesium salt is precipitated from cold solutions, although it is relatively soluble in hot solutions. It is an interesting fact that in the presence of high concentrations of magnesium, precipitation of the normally insoluble calcium compound is completely prevented. The reason for this effect is not understood.

Procedure. Place a drop of the solution to be tested on a black spot plate, and add a small particle of the reagent. In the absence of calcium, the reagent dissolves completely with the formation of a clear solution; but if calcium is present, a white precipitate of the calcium compound is formed. A blank test with distilled water is used in detecting small quantities of calcium. By this method, 0.01γ of calcium can be detected at a concentration limit of 1:5,000,000.[2]

Dihydroxytartaric acid osazone has also proved useful for the rapid differentiation between tap and distilled water. When the reagent is dissolved in the latter the resulting solution remains clear, but when dissolved in tap water the formation of the insoluble calcium salt may be observed. In this way one part of tap water is detected in 30 parts of distilled water. Some confusion may result if the mixture is warmed in the presence of ammonia or ammonium salts, since under these conditions a condensation product of the dihydroxytartaric acid osazone may separate from the solution.

Dubsky[6] has investigated the salts formed with dihydroxytartaric acid osazone and iron, bismuth and copper.

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3. F. Feigl, *Rec. trav. chim.* 58, 471-80 (1939); *C.A.* 33, 5771 (1939).
4. F. Feigl, *Chem. and Ind.* 1161-5 (1938).

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7. P. W. West, *J. Chem. Ed.* 18, 528-32 (1941); *C.A.* 36, 718 (1942).

m-NITROBENZOIC ACID

$C_7H_5O_4N$ Mol. Wt. 167.12 Beil. Ref. IX, 376.

$O_2N—C_6H_4—CO_2H$

Use: Detection and determination of thorium.

m-Nitrobenzoic acid is a white or slightly yellow crystalline solid. It melts at 140-142° C. One g. of the solid dissolves in 320 ml. of water, 3 ml. of alcohol, 4 ml. of ether, 18 ml. of chloroform, approximately 2 ml. of methyl alcohol, 2.5 ml. of acetone, and it is very slightly soluble in benzene.

Preparation: Mix 40 g. of benzoic acid and 80 g. of potassium nitrate and carefully powder the mixture. Warm 100 ml. of concentrated sulfuric acid to 70° C. and stir mechanically while the mixture of benzoic acid and potassium nitrate is added slowly at such rate that the temperature does not exceed 80° C. After the addition of the solid, raise the temperature to 90° C. and keep at this temperature until the nitrated acid separates on the surface as an oily liquid. Cool and separate the solid material. Distill with steam to remove benzoic acid and heat the residue to boiling and make slightly alkaline with a solution of barium hydroxide. Add 2 liters of water and heat to boiling by passing steam into the mixture. Cool and filter off the barium salt, which is decomposed with hot dilute hydrochloric acid. Recrystallize the precipitated acid from water.[1]

Detection and determination of thorium. Thorium is precipitated from a solution of its salts by the addition of an aqueous solution of *m*-nitrobenzoic acid. This reaction has been used by Neish [2] and by Kolb and Ahrle [3,5] for the determination of thorium, and for the separation of thorium from cerium, lanthanum, praseodymium and neodymium. The following procedure is used for the determination of thorium:

Reagent. Dissolve 3.5-4.0 g. of *m*-nitrobenzoic acid in a liter of water that has been heated to 80° C. Allow the mixture to stand overnight and filter.

Procedure. To 25 ml. of a solution containing about 0.1 g. of ThO_2, add approximately 150 ml. of the above reagent with stirring. Heat on a water bath to 60-80° C. for 15 minutes and filter. Wash first by decantation and finally on filter paper with a 5 per cent solution of the precipitant. Place the moist paper and the residue in a weighed platinum crucible, carefully heat with the cover off, then with the full flame of a Bunsen burner until white, and then covered for 15 minutes with a blast lamp. Weigh as ThO_2.

Beryllium, gadolinium, yttrium, titanium and samarium give no precipitates under the conditions of the above determination. Erbium is quantitatively precipitated, and zirconium, mercury and tin are also precipitated. For the complete separation of thorium from cerium, lanthanum, praseodymium and neodymium, it is necessary to re-precipitate the thorium compound two or perhaps three times.

Procedure. Dissolve the precipitate on the paper with 1:5 nitric acid, wash the paper with hot water, dilute the filtrate to 150 ml., and add 25 ml. of the reagent. Add methyl orange until the solution is red and then add dilute 1:10 ammonia slowly from a buret until the color changes from a deep to a light red or pink. As the precipitate becomes flocculent, add the ammonia dropwise with stirring, and then add an additional 50 ml. of the precipitant. From this point treat as described in the above procedure.

Wenger and Duckert [4] claim that *m*-nitrobenzoic acid is not sufficiently sensitive to be of great value as a reagent for thorium.

1. *Organic Synthesis,* Collective Vol. I, 1st ed., p. 383, John Wiley, New York (1932).
2. A. C. Neish, *J. Am. Chem. Soc.* **26,** 780 (1904).
3. A. Kolbe and H. Ahrle, *Z. angew. Chem.* **18,** 92 (1905).
4. P. Wenger and R. Duckert, *Helv. Chim. Acta.* **25,** 1110-14 (1942).
5. B. Justel, *Die Chemie.* **56,** 157-8 (1943).

p-NITROBENZOIC ACID

$C_7H_5O_4N$ Mol. Wt. 167.12 Beil. Ref. IX, 389.

$$O_2N—C_6H_4—CO_2H$$

Use: Alkalimetric standard.

p-Nitrobenzoic acid separates from solution in the form of white scales. It is readily purified by two or three recrystallizations from ethyl alcohol. The pure crystals melt at 242.4° C. These are only sparingly soluble in water and alcohol but are soluble in ether and chloroform.

Preparation: Place 11.5 g. of *p*-nitrotoluene, 34 g. of coarsely powdered sodium dichromate, and 75 ml. of water in a one-half liter flask which is provided with a mechanical stirrer, and with the stirrer running, add dropwise from a separatory funnel 46 ml. of concentrated sulfuric acid. Add the sulfuric acid at such rate that the mixture does not become hot enough to distill off the *p*-nitrotoluene. After the sulfuric acid has been added, boil the contents of the flask gently, with reflux, for one-half hour and allow the mixture to cool. Add 100 ml. of water and filter through cloth and wash with an additional 50 ml. of water. Digest the crude, dark yellow product on a water-bath with 50 ml. of 5 per cent sulfuric acid for a short time, allow to cool, filter, and dissolve in about 150 ml. of a warm 5 per cent solution of sodium hydroxide. Sufficient sodium hydroxide solution should be added so that the liquid remains alkaline after shaking. Cool and filter, and acidify the filtrate with dilute sulfuric acid by pouring the alkaline solution into the sulfuric acid. Again filter, wash the precipitate well with water, and dry on a porous plate in a vacuum desiccator. Recrystallize from benzene, alcohol or boiling water.[1]

Alkalimetric standard. *p*-Nitrobenzoic acid may be used as an accurate primary standard in neutralization processes. The compound is readily obtained pure by recrystallizing several times from ethyl alcohol. It is not bulky, it has a high equivalent weight (167.12), it requires a drying temperature only of 120° C., and it is not excessively hygroscopic.[2]

1. *Organic Synthesis,* Collective Vol. I, 2nd ed., p. 392, John Wiley, New York (1941).
2. W. M. Thornton and D. Getz, *Am. J. Sci.* 9, 176-80 (1925); *C.A.* 19, 1233 (1925).

2-NITRO-4-SULFOBENZOIC ACID

$C_7H_5O_7NS$ Mol. Wt. 247.17 **Beil. Ref. XI, 391.**

$HO_3S—C_6H_3(NO_2)—CO_2H$

Use: Alkalimetric standard.

Preparation: Sulfonate *o*-nitrotoluene by adding gradually to fuming sulfuric acid in the proportion of 1-2 volumes of acid to every volume of *o*-nitrotoluene used. Heat the mixture on a water-bath for a few minutes to complete the sulfonation, and then dilute with water. Heat nearly to boiling, neutralize with calcium carbonate and filter while hot from the precipitated calcium sulfate. Precipitate the calcium in the hot filtrate with potassium carbonate and again filter. Evaporate the filtrate, which contains 2-nitro-4-toluenesulfonic acid, until crystals appear, and allow the mixture to cool.

Dissolve 10 parts by weight of the 2-nitro-4-toluenesulfonic acid and 3 parts by weight of potassium hydroxide in 500 parts of water and heat the mixture on a water-bath, and then add 22 parts by weight of finely powdered potassium permanganate. Heat on a water-bath for 8-10 hours and add a small quantity of alcohol to decompose any unchanged potassium permanganate. Filter and evaporate the filtrate to a small volume. Cool, strongly acidify with concentrated hydrochloric acid, and purify the crystalline product which forms by crystallizing from water containing animal charcoal.[1]

Use as an alkalimetric standard. Kastle[2] has used 2-nitro-4-sulfo-benzoic acid as a standard in acidimetry. It is easily prepared in a pure state. It is anhydrous and can be dried in air with the aid of heat, or over sulfuric acid in a vacuum desiccator. It is stable in air under ordinary conditions and is not hygroscopic or deliquescent. It gives a sharp end-point with phenolphthalein.

1. E. Hart, *Am. Chem. J.* 1, 340-356 (1879-80).
2. J. H. Kastle, *Am. Chem. J.* 44, 487-93 (1910).

SULFONDIACETIC ACID

$C_4H_6O_6S$ Mol. Wt. 182.15 **Beil. Ref. III, 253(97).**

$HO_2C—CH_2—SO_2—CH_2—CO_2H$

Use: Detection of barium, lead, mercury and silver.

Sulfondiacetic acid is a crystalline solid melting at 182° C. It is readily soluble in water and in alcohol, but is only slightly soluble in ether.

Preparation: Neutralize a solution of 1 part of thiodiglycolic acid with an alkali carbonate, and add alternately a 5 per cent solution of potassium permanganate and 2 parts of thiodiglycolic acid in small quantities so that the reaction mixture always remains as nearly neutral as possible. As soon as the permanganate color persists for a few minutes, filter and concentrate the filtrate by evaporation. Precipitate oxalic acid by addition of calcium chloride and filter. Finally precipitate sulfondiacetic acid by the addition of barium chloride. Separate the barium salt and decompose with dilute sulfuric acid. Filter off the barium sulfate and collect the crystals which form in the concentrated filtrate.[1]

Reactions. Sulfondiacetic acid reacts to form an instantaneous precipitate with mercurous and barium salts. Colorless crystals are slowly formed with silver and lead salts, and a white precipitate is obtained with mercuric salts. Other cations are not precipitated, even after the addition of sodium acetate or ammonia. The acid does not form internal complexes with the cations.[2]

1. J. M. Loven, *Ber.* 17, 2818 (1884).
2. J. V. Dubsky, M. Hrdlicka, A. Okac and V. Sindelar, *Chem. Obzor.* 15, 21-2 (1940); *C.A.* 34, 6185 (1940).

THIODIGLYCOLIC ACID

$C_4H_6O_4S$ Mol. Wt. 150.15 Beil. Ref. III, 253(97)

$$HO_2C—CH_2—S—CH_2—CO_2H$$

Use: Detection of copper, lead, mercury and silver.

Thiodiglycolic acid is a crystalline solid melting at 129° C. It is soluble in water and alcohol.

Preparation: Dissolve 45 g. of sodium hydroxide in sufficient water to make 100 ml. of solution, and saturate one-half of this solution with hydrogen sulfide. Pour this solution simultaneously with the other half into a solution of sodium chloroacetate which is formed by adding a solution of 145 g. of crystalline sodium carbonate in 50 ml. of water, warmed to 35° C., to 95 g. of monochloroacetic acid. Allow to stand for 3 hours and mix carefully with 110 g. of concentrated sulfuric acid. Filter the warm solution and allow to stand for 6 hours. Filter with suction and recrystallize from about five-sevenths as much hot water.[1]

Reactions. Thiodiglycolic acid forms colorless crystals of $S(CH_2CO_2)_2HK$ and $S(CH_2CO_2H)_2 \cdot S(CH_2CO_2)_2HK$. A yellow precipitate of $S(CH_2CO_2Ag)_2$ is formed with silver nitrate. A white precipitate is also obtained with lead acetate and with mercurous salts, and a dark violet precipitate is obtained with copper. A cloudy solution is obtained with barium. The reagent does not react with other cations.

A 0.02 M solution of the thiodiglycolic acid reacts with a 0.02 M solution of copper sulfate or copper acetate to form a blue precipitate of $S(CH_2CO_2)_2Cu$. In solution the copper compound decomposes with the formation of a labile yellow cuprous salt, which readily forms a stable dark violet cupro-cupric salt.

The reagent does not form internal complexes with the cations.[2]

1. J. M. Loven, *Ber.* 27, 3059 (1894).
2. J. V. Dubsky, M. Hrdlicka, A. Okac, and V. Sindelar, *Chem. Obzor.* 15, 21-2 (1940); *C.A.* 34, 6185 (1940).

CHAPTER VI

ACYL HALIDES

The reaction of acyl halides with water has been utilized for the determination of water in organic liquids. Acyl halides react with water to form the hydrogen halide and the organic acid. By titrating the hydrogen halide formed in the reaction, it is possible to determine indirectly the quantity of water present in an organic liquid.

The addition of acetyl chloride to an aqueous solution is a convenient method for saturating the solution with hydrogen chloride. This procedure has some application in analytical chemistry.

ACETYL CHLORIDE

Synonym: Ethanoyl chloride

C_2H_3OCl Mol. Wt. 78.50 Beil. Ref. II, 173.

CH_3—CO—Cl

Use: Determination of aluminum, barium and water.

Separation of aluminum and barium.

Acetyl chloride is a colorless, inflammable liquid. It has a pungent odor, and is extremely irritating to the eyes. Its sp. gr. is 1.104, and it boils at 52° C. It reacts violently with alcohol and water, but is miscible with benzene, chloroform, ether and glacial acetic acid.

Preparation: Place 90 g. glacial acetic acid in a distilling flask, and from a separatory funnel run in 72 g. of phosphorous trichloride, while cooling the flask in water. Fit the flask with a condenser and warm in a water-bath to 40-50° C. until the vigorous evolution of hydrogen chloride slackens and the liquid separates into two layers. Distill acetyl chloride on a boiling water-bath and purify by redistilling. Collect the fraction boiling at 51° C.[1]

Separation and determination of aluminum. The addition of acetyl chloride to an aqueous solution is a convenient method of saturating the solution with hydrogen chloride. A solution of acetyl chloride in acetone is used for this purpose in order to diminish the violence of the reaction. Aluminum chloride, $Al_2Cl_6 \cdot 6H_2O$, is completely precipitated by treating a solution of an aluminum salt with a mixture composed of 4 parts of acetone and 1 part of acetyl chloride, and after careful drying this precipitate is converted by ignition to Al_2O_3.[2] This reaction is used for the separation of aluminum and iron:

Procedure. Evaporate a solution containing both iron and aluminum dissolved in hydrochloric acid to the smallest possible volume, cool to about 15° C., and treat with 15-20 ml. of the 4:1 acetone-acetyl chloride mixture.

This reagent should be added dropwise to the solution of iron and aluminum with constant stirring. Filter through a Gooch crucible, wash with the precipitating mixture, and dry carefully for 10-15 minutes high above a low Bunsen flame. Gradually increase the flame to its full height to complete the ignition, and then weigh the residue as aluminum oxide.

To obtain satisfactory results in this determination, the reagent must be free of phosphorus.

Determination of beryllium. Beryllium may be determined by a method similar in all details to that employed in determining aluminum (see above).[3]

Separation and determination of barium. A procedure based on the action of a 4:1 mixture of acetone and acetyl chloride upon a concentrated solution of the chlorides of barium, calcium and magnesium affords a convenient and exact means of separating and determining barium when associated with calcium and magnesium, but it is not recommended for the separation of barium from strontium (see determination of aluminum above).[4]

Procedure. Cool a concentrated solution of chlorides (about 0.1 g. $BaCl_2$ and not more than 0.5 g. $MgCl_2$ and $CaCl_2$ in about 2 ml. of water) to about 15° C., and add 30 ml. of a 4:1 mixture of acetone and acetyl chloride from a dropping funnel at the rate of 5 drops per second, shaking constantly. Filter on asbestos through a Gooch crucible, wash with acetone, dry in an air-bath at 135° C., or at a low red heat, and finally weigh as $BaCl_2$. Results are said to be excellent.

Determination of water in organic media. In the presence of pyridine, acetyl chloride reacts quantitatively with water to produce 2 moles of titratable acid (actually present as pyridine salt), while only 1 mole of titratable acid is formed when the acetyl chloride reacts with alcohol. The equations illustrating these reactions are:

$$C_5H_5N \cdot CH_3COCl + H_2O \rightarrow C_5H_5N \cdot HCl + CH_3CO_2H$$

$$C_5H_5N \cdot CH_3COCl + ROH \rightarrow C_5H_5N \cdot HCl + CH_3CO_2R$$

Smith and Bryant[5] have used these reactions for determining the quantities of water present in samples of alcohols and other organic liquids. The reaction yields 97-98 per cent of the theoretical quantity of acid, and is satisfactory with as little as 2.0 mg. of water. An accuracy of 1.0 per cent is claimed.

Reagent. Mix 118 ml. of acetyl chloride with pure, anhydrous toluene to make 1 liter of solution.

Procedure. Pipet 10 ml. of the reagent into a 250-ml. volumetric flask. Place the flask in a beaker containing crushed ice. Allow to stand 1 minute and add 2 ml. of pyridine. Stopper and shake thoroughly. Now add the material to be analyzed in such quantity that 0.5 mole of acetyl chloride remains for each mole which reacts with water. Shake vigorously.

Allow the mixture to stand 2 minutes at room temperature. Decompose the excess reagent with absolute ethyl alcohol (or methyl alcohol), added in two portions. Add the first ml. of the alcohol from a pipet and shake. Allow to stand 5 minutes and add an additional 25 ml. of absolute alcohol. Let stand 10 minutes at room temperature, and titrate with 0.5 N sodium hydroxide to an end-point with phenolphthalein.

1. A. Bechamp, *Compt. rend.* 40, 944 (1855) ; 42, 224 (1856).
2. H. D. Minnig, *Am. J. Sci.* **39**, 197-200 (1915) ; *C.A.* **9**, 771 (1915).
3. H. D. Minnig, *Am. J. Sci.* 40, 482-5 (1915) ; *C.A.* 10, 319 (1916).
4. F. A. Gooch and C. N. Boynton, *Am. J. Sci.* 31, 212-18 (1911) ; *C.A.* **5**, 1718 (1911).
5. D. M. Smith and W. M. D. Bryant, *J. Am. Chem. Soc.* **57**, 841 (1935).

CINNAMOYL CHLORIDE

C_9H_7OCl Mol. Wt. 166.61 Beil. Ref. IX, 587(233).

$$C_6H_5—CH=CH—CO—Cl$$

Use: Determination of water.

Cinnamoyl chloride is a yellowish crystalline solid. It melts at 35-36° C. and boils at 170-171° C. at 58 mm. pressure. It is soluble in chloroform.

Preparation: Cinnamoyl chloride is prepared by the reaction between equal molecular quantities of cinnamic acid and phosphorous pentachloride, and the subsequent distillation of phosphorous oxychloride from a water-bath under reduced pressure. A brown oil is obtained which may be distilled without decomposition *in vacuo.* The compound crystallizes in the receiver into a yellow solid.[1]

Determination of water. van Nieuwenburg [2] has used cinnamoyl chloride for the titrimetric determination of small quantities of water, and he reports that this acid halide is the most satisfactory of all of those tried. The reagent reacts with water according to the following equation:

$$2C_8H_7COCl + H_2O \rightarrow C_8H_7—CO_2—CO—C_8H_7 + 2HCl$$

All of the hydrogen chloride which is formed in this reaction is removed from the mixture at 60-70° C. by means of a current of air. The gas is trapped in water, and the resulting solution is titrated with a standard base according to the usual procedure. With an alkali hydroxide solution, the original chloride and the anhydride which is formed are not appreciably volatile even at 110° C. Cinnamoyl chloride, therefore, has been found to possess distinct advantages over naphthyloxychlorophosphine which has also been used for this purpose.

Lindner and Zienert [3], however, prefer naphthoxychlorophosphine. As one of the advantages of this reagent, they claim that it possesses better keeping qualities than cinnamoyl chloride.

1. L. Claisen and P. J. Antweiler, *Ber.* **13**, 2124 (1880).
2. C. J. van Nieuwenburg, *Mikrochim. Acta.* 1, 71-4 (1937) ; *C.A.* **31**, 5717 (1937).
3. J. Lindner and G. Zienert, *Mikrochem. ver. Mikrochim. Acta.* 31, 254-62 (1943) ; *C.A.* **39**, 2708 (1945).

CHAPTER VII

ACID ANHYDRIDES

The acid anhydrides react with water to form an equivalent quantity of the corresponding acid. By determining the quantity of acid formed in this reaction, it is possible to determine the amount of water present in samples of organic liquids. A few anhydrides have been used for this purpose. Some anhydrides have also been studied as alkalimetric standards.

ACETIC ANHYDRIDE

$C_4H_6O_3$ Mol. Wt. 102.09 Beil. Ref. II, 166.

$$CH_3—CO—O—OC—CH_3$$

Use: Determination of water content of acetic acid, cotton or starch.

Acetic anhydride is a colorless, very refractive liquid. It possesses a strong acetic acid odor. Its sp. gr. is 1.080. It melts at −73° C., and boils at 139° C. It dissolves slowly in water with the formation of acetic acid, and in ethyl alcohol with the formation of ethyl acetate. It is soluble in chloroform, ether, and pyridine.

Preparation: Allow 54 g. of acetyl chloride to flow dropwise, from a separatory funnel onto 80 g. of finely powdered anhydrous sodium acetate which is contained in a distilling flask fitted with a condenser. When about half of the acetyl chloride has been run into the flask, interrupt the addition and stir the reaction mixture. Then continue the addition of acetyl chloride at such rate that none distills over. Distill the anhydride from the flask by heating with a luminous flame kept constantly in motion. Add 3 g. of finely powdered, anhydrous sodium acetate to the distillate, and fractionally distill. Collect the fraction boiling at 138° C. The anhydrous sodium acetate is obtained by fusing the hydrate in an iron dish.[1]

Determination of water. The water content of cotton or starch may be determined with acetic anhydride, using the process of Mitra and Venkataraman.[2] The sample is distilled with toluene or xylene into a known volume of solution of acetic anhydride in pyridine. When hydration is complete, the mixture is treated with aniline, which yields one mole of acetic acid and one mole of acetanilide for each mole of acetic anhydride. An aliquot is then titrated with a standard base. If X moles of acetic anhydride are used, Y moles of water yield $X + Y$ moles of acetic acid.

Acetic anhydride is also used with camphoric acid to determine the water content of acetic acid.[3] For details of this procedure see section on camphoric acid.

1. C. Gerhardt, *Ann. Chim.* [3] **37**, 313 (1853).
2. N. C. Mitra and K. Venkataraman, *Current Sci.* **5**, 199-200 (1936); *C.A.* **31**, 967 (1937).
3. Q. Toennies and M. Elliott, *J. Am. Chem. Soc.* **59**, 902-6 (1937); *C.A.* **31**, 6581 (1937).

BENZOIC ANHYDRIDE

$C_{14}H_{10}O_3$ Mol. Wt. 226.22 Beil. Ref. IX, 164.

$C_6H_5—CO—O—OC—C_6H_5$

Use: Determination of water in organic liquids.

Benzoic anhydride is a white, almost colorless, crystalline powder. It is only slowly decomposed by cold water or cold alkali. It melts at 42° C. and boils at 360° C. It is insoluble in water, but dissolves in alcohol, chloroform, acetone, benzene and ether.

Preparation: Place 1500 g. of benzoic acid, 1390 ml. of acetic anhydride and 1 ml. of sirupy phosphoric acid in a 5-liter flask, and fit with a two-holed stopper carrying a 90-cm. fractionating column and a dropping funnel. Distill the mixture slowly at such rate that the temperature of the vapor at the head of the column does not rise above 120° C. Continue the distillation until 250 ml. of distillate has passed over, then add 250 g. of acetic anhydride, and again distill. When a second 250-ml. portion of distillate has passed over, add an additional 250 g. of acetic anhydride, and continue the distillation. Collect three fractions as follows: (a) that distilling below 120° C., (b) between 120° and 130° C., and (c) between 130° and 140° C. Continue heating until the temperature of the mixture in the flask rises to 270° C.

Fractionally distill the residue under reduced pressure and collect fractions boiling respectively at 19-20 mm. as follows: (a) below 165° C., (b) at 165-210° C. and (c) at 210-220° C.

Mix the lower fractions with the fraction boiling at 120-130° C., add 1 drop of phosphoric acid, and distill as before to collect an additional quantity of the fraction boiling at 210-220° at 20 mm. This fraction contains the crude benzoic anhydride. The lower-boiling fractions may be redistilled until they become too small to justify additional treatment.

Redistill the fraction which boils at 120-130° C. under atmospheric pressure to yield an additional quantity of acetic acid (fraction boiling below 120° C.) and acetic anhydride (fraction boiling at 130-140° C.).

Dissolve the crude product in benzene, using 50 ml. of the solvent for each 100 g. of benzoic anhydride. Add just sufficient petroleum ether (about 100 ml.) to cause a cloudiness, and then chill the mixture. Pure benzoic anhydride separates as colorless crystals which melt at 43° C.

Free the mother liquors of solvent by distillation on a water bath, and distill the residue under reduced pressure. Collect the fraction boiling at 210-220° C. under 20 mm. pressure, and treat as before to collect an additional quantity of benzoic anhydride. This process may be repeated once or twice more to improve the yield.[1]

Determination of water in organic liquids. When benzoic anhydride is heated with a mixture of water and alcohol, the following reactions occur:

$$Bz_2O + H_2O \rightarrow 2BzOH,$$

and

$$Bz_2O + ROH \rightarrow BzOH + Bz{-}O{-}R$$

$$(Bz = \text{benzoyl, } C_6H_5{-}CO{-})$$

These reactions are quantitative and complete after heating the mixture for a few hours at 110° C. On cooling, the total benzoic acid liberated is determined by titration. If the equivalent or molecular weights of the alcohols present are known, then the weight of the water can be calculated after titration.[2] The slight solubility and the low rate of hydrolysis of benzoic anhydride in cold water makes possible the accurate titration of an aqueous solution of benzoic acid in the presence of free benzoic anhydride at 0-10° C.[3] The determination of water in organic liquids based on the use of benzoic anhydride is precise and useful, but is time consuming.

1. *Organic Synthesis,* Collective Vol. I, 2nd, p. 91, John Wiley, New York (1941).
2. J. Ross, *J. Soc. Chem. Ind.* **51**, 121T (1932).
3. B. H. Wilsdon and N. V. Sidgwick, *J. Chem. Soc.* **103**, 1971 (1913).
4. H. T. Clarke and E. J. Rahrs, *Ind. Eng. Chem.* **15**, 349 (1923).

PHTHALIC ANHYDRIDE

$C_8H_4O_3$ Mol. Wt. 148.11 Beil. Ref. XVII, 469.

$$C_6H_4(CO)_2O$$

Use: Alkalimetric standard.

Phthalic anhydride consists of lustrous white needles. It melts at 130.8° C. It is only slightly soluble in cold water, but dissolves more readily in hot water with conversion to phthalic acid. It is soluble in alcohol but is only sparingly soluble in ether.

Preparation: *Phthalic acid:* Mix 15 g. of naphthalene, 7.5 g. of mercuric sulfate and 120 ml. of concentrated sulfuric acid in a retort, and heat gently with occasional shaking until the naphthalene layer dissolves. Fit the end of the retort to a condenser, which in turn is provided with a receiver containing 100 ml. of water, and cooled in cold water.

Heat the retort, cautiously at first, and then strongly to distill the contents. Oxidation becomes vigorous as the temperature of the liquid rises to the boiling point. Some naphthalene distills at first, and crystals of phthalic anhydride form in the condenser. Phthalic acid collects in the receiver. Continue the distillation until the residue becomes dry. Allow the contents of the receiver to become cold, filter, wash, and dissolve in sodium hydroxide. Remove any undissolved naphthalene by filtration, and reprecipitate the acid by adding hydrochloric acid. Recrystallize from water or dilute alcohol.

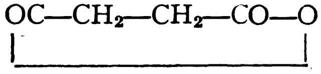
Phthalic anhydride: Phthalic anhydride is obtained by subliming phthalic acid.

Standards of alkalimetry. Phthalic anhydride has been proposed as a standard in alkalimetry, but it appears to be less satisfactory than many other compounds which have been used.[1]

[1] I. K. Phelps and L. H. Weed, *Am. J. Sci.* **26**, 138-42 (1908); *C.A.* 2, 2659 (1908).

SUCCINIC ANHYDRIDE

$C_4H_4O_3$ Mol. Wt. 100.07 Beil. Ref. XVII, 407.



$OC—CH_2—CH_2—CO—O$

Use: Alkalimetric standard.

Succinic anhydride is a white crystalline compound. It melts at 120° C. and boils at 261° C. It is soluble in water, alcohol, ether and chloroform.

Preparation: Treat 10 g. of finely powdered succinic acid with 20 g. of acetyl chloride and heat on a water-bath at 60° C. with a return condenser as long as bubbles of gaseous hydrogen chloride are evolved. Cool, separate the crystals which form and recrystallize from ethyl acetate. Wash with absolute alcohol and dry to constant weight over sulfuric acid.[1]

Alkalimetric standard. Phelps and Weed[1] report that succinic anhydride is excellent for the standardization of 0.1 N solutions of bases, such as sodium hydroxide and barium hydroxide. Succinic anhydride dissolves only slowly in water, and the mixture should be heated until the reagent is completely dissolved before the addition of the alkali.

[1] I. K. Phelps and L. H. Weed, *Am. J. Sci.* **26**, 138-42 (1908); *C.A.* 2, 2659 (1908).

[2] I. M. Kolthoff, *Volumetric Analysis*, Translated by Furman, Vol. I (1928), and Vol. II (1929), John Wiley, New York.

CHAPTER VIII

ESTERS

The esters are not well represented among the organic compounds used in inorganic analysis. The only applications which have been reported are as solvents and wash liquids.

AMYL ACETATE

Synonym: Isoamylacetate

Use: Detection of chromium.

Amyl acetate (Beil. ref. II, 132) is a colorless, neutral liquid which possesses a pear-like odor and taste. Its sp. gr. is 0.876. Pure isoamyl acetate boils at 142°, although the commercial product, which is usually a mixture of various isomeric pentyl acetates, boils between 120° and 145°. The refractive index is 1.400 and the flash point is 25°. The ester is soluble in 400 parts of water, but is miscible with alcohol, ether, ethyl acetate, and amyl alcohol.

Detection of chromium. Bishop and Dwyer[1] claim that amyl acetate is the best solvent for the extraction of the blue color of the perchromic acids obtained in the reaction between hydrogen peroxide and soluble chromates in an acid solution. With the aid of amyl acetate, 0.002 mg. of chromium may be detected.

1. W. B. S. Bishop and F. P. Dwyer, *Australian Chem. Inst. J. and Proc.* **2**, 278-80 (1935); *C.A.* **30**, 4781 (1936).

n-BUTYL ACETATE

$C_6H_{12}O_2$ Mol. Wt. 116.16 Beil. Ref. II, 130.

$$CH_3—CO—O—CH_2—CH_2—CH_2—CH_3$$

Uses: Detection of thallium, tin and tungsten.

Determination of molybdenum and rhenium.

n-Butyl acetate is a colorless liquid, boiling at 125-126° C. and solidifying at −77° C. Its sp. gr. is 0.8826. It is soluble in 120 parts of water, and is miscible with alcohol.

Determination of molybdenum and rhenium. The amber to reddish-brown color of molybdenum thiocyanate has been used for the colorimetric determination of small quantities of molybdenum in steel. The colored compound is soluble in ether, *n*-butyl acetate[1] and cyclohexanol.[2,3] Methods based upon the extraction of molybdenum by means of organic solvents have proved useful for the determination of molybdenum in various materials. Both *n*-butyl acetate and cyclohexanol are better solvents for the molybdenum thiocyanate or the rhenium thiocyanate complexes than ether or ether mixtures. *n*-Butyl acetate appears to be superior to cyclohexanol for the molybdenum extraction, since hydrolytic products do not cause a color fading. Heppell[4] has developed a scheme for the rapid analysis of steel in which molybdenum is separated from other metals by extraction with *n*-butyl acetate. Stanfield[5] has used a similar method for the determination of molybdenum in plants and soils.

Detection of tungsten and tin. *n*-Butyl acetate is used indirectly in the detection of tungsten and tin with dithiol for the removal of interference by molybdenum and vanadium. For details of this method, see section on dithiol. Molybdenum is extracted as the complex thiocyanate as a preliminary to the test for tungsten and tin. Vanadium is separated similarly.[6]

Separation of thallium. In a systematic scheme of analysis of the thallium group, consisting of lead, silver, thallium, and bismuth, Miller[7] separates thallium as thallium bromide from the other ions by extracting with *n*-butyl acetate.

1. L. H. James, *Ind. Eng. Chem., Anal. Ed.* 4, 89-90 (1932).
2. L. C. Hurd and F. Reynolds, *Ind. Eng. Chem., Anal. Ed.* **6**, 477-8 (1934); *C.A.* **29**, 421 (1935).
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4. D. H. H. Heppell, *Ind. Chemist.* **16**, 173 (1940); *C.A.* 34, 5784 (1940).
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6. C. C. Miller and A. J. Lowe, *J. Chem. Soc.* 143, 1258-66 (1940).
7. C. C. Miller, *J. Chem. Soc.* 72-5 (1941); *C.A.* **35**, 4305 (1941).

ETHYL ACETATE

$C_4H_8O_2$ Mol. Wt. 88.10 Beil. Ref. II, 125.

$CH_3—CO—O—C_2H_5$

Uses: Detection of bismuth, gold, iron, mercury, oxidizing agents and platinum.

Determination of bismuth, boron, gold, iron, molybdenum, platinum, potassium and scandium.

Ethyl acetate is a colorless, clear, volatile liquid, which possesses a characteristic fruity odor. It is decomposed slowly by moisture and eventually exhibits an acid reaction. It boils at 77° C. and has a sp. gr. of 0.900. One ml. of the liquid dissolves in 10 ml. of water, although it is less soluble in water at higher temperatures. It is miscible with alcohol, acetone, chloroform and ether.

Determination of potassium. Ethyl acetate has been used in analytical chemistry principally as a solvent and for the extraction of various materials. Among the most important of these uses is the analysis of the alkali metals. Many solvents, especially the alcohols, have been investigated to determine their solvent effects upon various salts of alkali and alkaline earth metals with a view of employing them for the separation of these metals. Smith[1] and Willard and Smith[2] have studied the solubility of the alkali and alkaline earth perchlorates in various solvents (see section on alcohols) including ethyl acetate.

Smith and Ross[3] have used ethyl acetate in a procedure for the separation of sodium and lithium from potassium. At 24° C., 100 ml. of pure ethyl acetate dissolves 1.1 mg. of potassium perchlorate and at 0° C. only 0.9 mg. The solubility of sodium perchlorate is about 9.6 g. in 100 g. of the solvent. The separation is carried out as follows:

Procedure. Convert the potassium, sodium and lithium chlorides to perchlorates by evaporating the solution with an excess of pure perchloric acid. Remove the excess perchloric acid by evaporating to dryness, then dissolve the residue in water and again evaporate to dryness. Extract lithium and sodium perchlorates by using a mixture of equal parts of *n*-butyl alcohol and ethyl acetate. Wash the residue of potassium perchlorate two times by decantation through a weighed Gooch crucible, then dissolve the residue in water and repeat the separation. Filter the purified potassium perchlorate through the same Gooch crucible, wash with the same solvent that was used in the extraction, dry at 350° C. and weigh.

The lithium and sodium in the filtrate are determined by a procedure described in the section on *n*-butyl alcohol.

Miller and Traves[4] have used a mixture of equal parts of *n*-butyl alcohol and ethyl acetate to extract the perchlorates of calcium, sodium and barium from a mixture of these metals with potassium. Potassium is then determined according to the method of Smith and Ross.[3]

Detection and determination of gold and mercury. Gold may be separated advantageously from other elements by extracting the chloride with ethyl acetate. Whitmore and Schneider[5] recommend the following procedure:

Procedure. To 0.5 ml. of the gold solution, contained in a small test tube, add 1 ml. of ethyl acetate and shake vigorously. Allow the mixture to settle and draw off the acetate layer with a small pipet. Extract the solution twice more with fresh portions of ethyl acetate, and carefully evaporate the ethyl acetate extracts to dryness. Dissolve the residue in a little water and dilute hydrochloric acid and test for gold with ammonium thiocyanate or by other well-known methods.

Miller and Lowe[6] have used ethyl acetate to separate gold and mercury from an analytical group consisting of gold, mercury, palladium, platinum and iridium.

Procedure. Evaporate a solution of these metals in aqua regia to about 0.1 ml. on a steam-bath, and treat the mixture with 3 ml. of water, 1 drop of N hydrochloric acid and 1.5 ml. of ethyl acetate. Repeat the extraction and evaporate the ethyl acetate extracts to dryness on a water-bath. Dissolve the residue in 3 N hydrochloric acid. This solution contains gold and mercury, which may then be detected by standard procedures.

Gold is separated from platinum and palladium by extracting the hydrochloric acid solution of their salts with ethyl acetate.[13] Platinum must be in the tetravalent state. For separating gold from palladium, the volume of the solution should be about 10 ml., and it should be about 6 N in hydrochloric acid. The gold is extracted by shaking the solution with an equal volume of ethyl acetate. The aqueous layer is removed, the extract washed with 6 N hydrochloric acid, and the solution extracted once more if it contains 5-10 mg. of gold or twice more with 20 mg. or more of gold. The washings are added to the original solution before repeating the extractions with ethyl acetate.

Determination of molybdenum. When an excess of sodium thiosulfate solution is added to a solution of a molybdate acidified with hydrochloric acid, a precipitate of sulfur is formed and molybdenum is reduced to form a colored compound which may be extracted with ether or ethyl acetate. The color of the solution in the organic solvent is suitable for colorimetric comparison against a series of standards.[14] The color varies with the molybdenum concentration from lilac to red-brown. A lilac color is obtained with 0.005 mg. and a red color with 5 mg. of molybdic acid. This reaction is more sensitive than those with stannous chloride, hydrogen peroxide or potassium xanthate. The color is destroyed by alkalies, but is not affected by tartaric, citric, oxalic or tannic acids, ammonium salts, chlorates, chromates and many cations. Copper and iron may interfere unless present in small quantities.

The following method is used for the determination of molybdenum in steel:[18]

Procedure. Dissolve 1-2 g. of steel in aqua regia and evaporate to dryness. Dissolve the residue in 10 ml. of concentrated hydrochloric acid, and dilute with 20-30 ml. of water. Filter, and dilute the filtrate to 100 ml.

Add 2 ml. of concentrated hydrochloric acid to 10 ml. of the sample solution, and extract with 8 ml. of a mixture of 80 per cent ethyl acetate and 20 per cent ether. Shake the solvent extract with an equal volume of 30 per cent sodium thiosulfate solution. Separate the two layers, and repeat the treatment with a second portion of sodium thiosulfate solution. Filter the solvent layer, and compare with a series of standards prepared from steels of known molybdenum content. Molybdenum may be added to the steel to give suitable standards.

The thiosulfate method for determining molybdenum has been recommended as superior to many other methods by Gillis.[19]

Determination of scandium. Scandium is separated from other metals by converting to the thiocyanate or benzoate and extracting with ethyl acetate. This procedure may be carried out as a preliminary to a final determination with morin.

Detection and determination of bismuth. Many analytical procedures have been based on the formation of a yellow to orange color when a solution of bismuth nitrate or sulfate is treated with an excess of potassium iodide.

Powell[7] recommends the following test for bismuth:

Procedure. To 10 ml. of the solution to be tested, add 2 ml. of dilute hydrochloric acid and 0.5 g. of potassium iodide. Mix and add 5 ml. of alcohol or acetone and 5-10 ml. of ethyl acetate. Shake and allow the liquids to separate. A red color appears in the upper layer if bismuth is present.

It is possible to render the test more sensitive, and also to eliminate interference, by extracting the colored compound with organic solvents such as ethyl acetate. In this way bismuth is separated from lead.[11] Haddock [15] recommends extracting the bismuth solution containing potassium iodide with a 3:1 mixture of amyl alcohol and ethyl acetate.

Trivalent bismuth reacts with potassium thiocyanate to form an intense yellow color which can be extracted from concentrated solutions with ethyl acetate and amyl alcohol.[12]

Detection and determination of platinum. The addition of stannous chloride to a solution of a platinum salt yields a red to brown color which is extracted with ether or ethyl acetate. When diluted with water, the red solution deposits a chocolate brown precipitate. The red solution turns dark red to black when heated.[8]

The extraction of chloroplatinous acid with ethyl acetate may be used for the separation of platinum from iron and copper, and also for the colorimetric determination of small quantities of platinum.[16] The aqueous solution must be 1 N in hydrochloric acid for complete extraction. By shaking 2 ml. of ethyl acetate with 10 ml. of 1:9 hydrochloric acid solution containing as little as 0.5γ of platinum and a little stannous chloride, a yellow color is obtained in the ester layer.

Detection and determination of iron. Ethyl acetate may be used to extract the color formed in the reaction between ferric iron and thiocyanate.[17]

Determination of boron. Halphen [9] has used ethyl acetate as a solvent for turmeric in a colorimetric method for the determination of boric acid:

Procedure. Separate boron as methyl borate and collect in 0.2 ml. of N sodium hydroxide. Evaporate to dryness in a small test tube and dissolve the residue in 1 ml. of water and 2 ml. of hydrochloric acid ($d = 1.162$). Standards containing known quantities of boric acid are similarly treated. Then to both standards and unknown add 1 ml. of an ethyl acetate solution of turmeric and allow to stand for 50 minutes and then compare.

Detection of oxidizing agents. Ethyl acetate is used as a solvent for 2,5-bis[2,4-dimethyl-N-pyrryl]-3,6-dibromohydroquinone, which is a reagent for oxidizing agents.[10]

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12. E. Tommila, *Acta Chem. Fennica.* **7B**, 79 (1934); *C.A.* **28**, 3334 (1934).
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17. R. Vanossi, *Anales soc. quim. argentina.* **29**, 48 (1941).
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19. J. Gillis, *Mikrochem. ver. Mikrochim. Acta* **31**, 58-68 (1943); *C.A.* **38**, 1979 (1944).

ETHYL MALONATE

$C_7H_{12}O_4$ Mol. Wt. 160.17 Beil. Ref. II, 573.

$$C_2H_5—O_2C—CH_2—CO_2—C_2H_5$$

Use: Detection of ammonia and potassium.

Etheyl malonate is a colorless liquid. It has a slight, but pleasant, odor. It boils at 198-199° C., and has a sp. gr. of 1.055. It is insoluble in water, but is miscible with alcohol and ether.

Preparation: Place 50 g. of chloroacetic acid and 100 ml. of water in a large evaporating dish and heat the mixture to 55-60° C. Add about 28 g. of anhydrous sodium carbonate until the evolution of carbon dioxide ceases and the liquid is neutral. Now add 28 g. of sodium cyanide, heat the mixture gently, and stir well. Remove the flame and allow the mixture to stand until the reaction subsides, and then rapidly evaporate on a sand-bath. During the evaporation the mass is stirred continuously with a thermometer, and when the temperature reaches 135° C. discontinue the evaporation. Allow the mass to cool, with stirring, and quickly break up the solid into a coarse powder. Place in a 500 ml. round bottom flask, and add 20 ml. of absolute alcohol. Fit the flask with a reflux condenser, and add a cold mixture of 80 ml. of absolute alcohol and 90 ml. of concentrated sulfuric acid over a space of about 10 minutes. Heat the flask for about 2 hours on a water-bath. Cool quickly, add 100 ml. of water, and filter off any insoluble material. Wash the filter several times with small quantities of ether and shake the filtrate with ether and separate. Repeat the extraction of the filtrate with another portion of ether, and unite the ether extracts. Shake these extracts, first with water, and then with a strong solution of sodium carbonate to remove any acids. Separate the ether extract, dry with calcium chloride, and remove the ether on a water-bath. Finally distill the ester under reduced pressure.[1,2]

Detection of ammonia. A saturated solution of picric acid in ethyl malonate, or in alcohol containing 5 per cent glycerol, may be used as a sensitive test for ammonia.[3] By this reaction, yellow, characteristic crystals are obtained. Less than 0.1 mg. of ammonia is detected in this way.

Detection of potassium. A saturated solution of picric acid in ethyl malonate has been used for the microdetection of potassium.[4]

1. M. Conrad, *Ann.* **204**, 126 (1880).
2. W. A. Noyes, *Am. Chem. J.* **18**, 1105 (1896).
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METHYL ACETATE

$C_3H_6O_2$ Mol. Wt. 74.08 Beil. Ref. II, 124.

$CH_3—CO—O—CH_3$

Use: Determination of lithium and sodium.

Methyl acetate is a colorless liquid which possesses a pleasant odor. It has a sp. gr. of 0.928 and boils at 57-59° C. It is soluble in water and is miscible with alcohol and ether.

Determination of the alkali metals. Methyl acetate may be used for the separation of lithium and sodium from potassium, rubidium, and cesium.[1] Lithium and sodium perchlorates are soluble in the ester while the perchlorates of potassium, cesium and rubidium do not dissolve. Lithium and sodium may be separated after extraction with methyl acetate by a method based on the difference in the solubility of their chlorides in amyl alcohol.

1. T. Kato, *J. Electrochem. Assoc. Japan.* **3**, 276-83 (1935); *C.A.* **30**, 2517 (1936).

POTASSIUM ETHYL SULFATE

$C_2H_5O_4SK$ Mol. Wt. 164.22 Beil. Ref. I, 325.

$KC_2H_5SO_4$

Use: Detection of borate.

Potassium ethyl sulfate is a white crystalline solid, which is readily soluble in alcohol or water.

Preparation: Mix equal molecular quantities of absolute alcohol and concentrated sulfuric acid and allow the mixture to stand for four hours on a water-bath. Cool, dilute with ice, and then with water, and while avoiding warming, neutralize with potassium carbonate. The yield may be improved by using 3 moles of ethyl alcohol and 1 mole of sulfuric acid.[1,2]

Detection of borate. Borate may be detected by the following procedure, using potassium ethyl sulfate:[3,4]

Procedure. Mix the substance to be tested in a small tube with an excess of potassium ethyl sulfate, and heat until vapors just begin to appear. When ignited these vapors burn with a green-edged flame if boric acid is present.

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2. J. P. Claesson, *J. prakt. Chem.* [2] **19**, 246 (1879).
3. V. Castellana, *Gazz. chim. ital.* **36**, 232 (1906).
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CHAPTER IX

THE AMINES

The amines possess a number of useful analytical properties, but among the most important are those depending on their basic characteristics. A base is defined as a substance capable of combining with protons. Many nitrogenous organic compounds possess this ability, due to the presence of the nitrogen atom, and consequently they behave in a manner analogous to that of ammonia. The most important of the organic bases are the amines.

The general reaction of the amines as bases is given by the equation

$$R_3N + H^+ \rightleftharpoons R_3NH^+$$

The cations formed in this reaction combine in varying degrees with hydroxyl ions, depending on the strength of the bases, to form unionized molecules similar to ammonium hydroxide.

$$R_3NH^+ + OH^- \rightleftharpoons R_3NHOH$$

Unless the hydroxyl compound so formed is completely unionized, these reactions result in a decrease in the hydrogen ion concentration, and a corresponding increase in the hydroxyl ion concentration.

According to the principle of equilibrium and the law of mass action,

$$\frac{[R_3NH^+][OH^-]}{[R_3NHOH]} = K_B$$

where K_B is the ionization constant of the base at a definite temperature. The ionization constants of a number of organic bases are given in Table 30.

One of the most important uses of organic bases in analytical chemistry is for the precipitation of insoluble hydroxides.[1,2] Britton [3,4] has determined the approximate pH at which a number of metallic hydroxides are precipitated. These values are given in Table 31.

More recently Bordoni [5] has determined the values given in Table 32.

Since the various metallic hydroxides are precipitaed over a wide pH range, it might be expected that organic bases would serve for the separation of certain of the metals. Many such separations have actually been developed, but various factors tend to complicate the separation process.[6] It is not difficult to separate hydroxides which are precipitated at widely different pH values, but where they lie close together, separation may be difficult or impossible.

The approximate pH of a pure aqueous solution of any weak base may be calculated by the equation

$$[H^+] = \frac{K_W}{\sqrt{K_B C_B}}$$

where K_B and C_B are the ionization constant and molar analytical concentration respectively of the base, and K_W is the ionization constant of water. From this equation the pH of the solution may be expressed as

$$pH = 14 + \tfrac{1}{2} \log K_B + \tfrac{1}{2} \log C_B$$

TABLE 30.—IONIZATION CONSTANTS OF BASES

Base	K_B at 25° C.
Ammonium hydroxide	1.8×10^{-5}
Aniline	4.6×10^{-10}
o-Anisidine	3.11×10^{-10}
n-Butylamine	4.09×10^{-4}
p-Chloroaniline	8.45×10^{-11}
Di-*n*-butylamine	2.05×10^{-3}
Diethanolamine	7.62×10^{-7}
Diethylamine	1.26×10^{-3}
Diethylbenzylamine	3.6×10^{-5}
Diethylaniline	3.65×10^{-8}
Diisoamylamine	9.6×10^{-4}
Diisobutylamine	4.8×10^{-4}
Dimethylamine	7.4×10^{-4}
Dimethylaniline	1.15×10^{-9}
Dimethylbenzylamine	1.05×10^{-5}
s-Diphenylguanidine	1.32×10^{-4}
Di-*n*-propylamine	1.02×10^{-5}
Ethanolamine	2.77×10^{-5}
Ethylamine	5.6×10^{-4}
Ethylenediamine	8.5×10^{-5}
Methylamine	5×10^{-4}
Methylaniline	7.12×10^{-11}
Methyldiethylamine	2.7×10^{-4}
α-Naphthylamine	9.9×10^{-11}
β-Naphthylamine	2×10^{-10}
o-Phenylenediamine	3.3×10^{-10}
Phenylhydrazine	1.62×10^{-3}
Piperidine	1.60×10^{-3}
n-Propylamine	4.70×10^{-4}
Pyridine	2.3×10^{-9}
Quinaldine	2.64×10^{-3}
Quinoline	1.0×10^{-9}
o-Toluidine	3.3×10^{-10}
m-Toluidine	5.5×10^{-10}
p-Toluidine	2×10^{-9}
Triethylamine	6.4×10^{-4}
Trimethylamine	7.4×10^{-5}
Tripropylamine	5.5×10^{-4}
Urea	1.5×10^{-14}

If the solution also contains some salt, the expression for the hydrogen ion concentration becomes

$$[H^+] = \frac{K_W C_S}{K_B C_B}$$

in which C_S is the molar analytical concentration of the salt, and the other symbols have the same significance as above. The pH of the salt solution is given by

$$pH = 14 + \log K_B + \log C_B - \log C_S$$

When the concentration of the base and salt are equal, or nearly so, a rough approximation of the hydrogen ion concentration is given by

$$[H^+] = \frac{K_W}{K_B}$$

and

$$pH = 14 + \log K_B$$

TABLE 31.—pH AT WHICH VARIOUS HYDROXIDES ARE PRECIPITATED

pH	Metallic Hydroxide	pH	Metallic Hydroxide
3	Iron (III), tin (II) and zirconium	7	Iron (II), lead and samarium
4	Thorium and uranium	8	Cadmium, cerium, cobalt, neodymium, nickel, praseodymium and yttrium
5	Aluminum	9	Lanthanum, manganese, mercury and silver
6	Beryllium, chromium, copper and zinc	11	Magnesium

TABLE 32.—pH AT WHICH VARIOUS HYDROXIDES ARE PRECIPITATED

Metallic Hydroxide	pH	Metallic Hydroxide	pH
Tin	2	Lead	6
Ferric	2	Nickel	6.7
Aluminum	4.1	Cadmium	6.7
Zinc	5.2	Cobalt	6.8
Chromium	5.3	Mercury	7.3
Copper	5.3	Manganese	8.7
Ferrous	5.5	Silver	9
Beryllium	5.7	Magnesium	10.5

In aqueous solutions of the salt of a base and a strong acid, the approximate hydrogen ion concentration is calculated from the equation

$$[H^+] = \sqrt{\frac{K_W C_B}{K_B}}$$

and

$$pH = 7 + \tfrac{1}{2} \log K_B - \tfrac{1}{2} \log C_B$$

Analytical reactions of amines. Many amines form complex crystalline compounds, often colored, with inorganic salts by coordination, and these are frequently used for the microchemical detection of the cations.

Aniline, for example, gives characteristic microcrystals with cyanides and thiocyanates, and salts of copper, cobalt, mercury, nickel, cadmium, molybdenum, zinc, tungsten and vanadium. Some nitrogenous bases have also been used advantageously as precipitants for nitrates and perchlorates.

Hydrogen cyanide may be detected by its catalytic effect in promoting the reaction between ammonia and alloxan to form characteristic crystals of oxaluramide. This reaction has been studied by Kozlovskii and Penner,[7] who have used various amines instead of ammonia. Many of these are claimed to have increased the sensitivity of the test.

The reducing properties of many amines have proved extremely useful in the detection and determination of oxidizing substances.[8] For example, benzidine and *o*-tolidine have been widely used for the detection and determination of cations capable of existing in more than one stable valence state, and also of oxidizing anions and molecules. These reactions are based on the formation of colored oxidation products.

Phosphorus and molybdenum are determined colorimetrically by reducing the phosphomolybdate with some substituted amines, such as 1-amino-2-naphthol-4-sulfonic acid.

The reaction between primary amines and nitrous acid to form diazo compounds, which are then coupled to aromatic amines and phenols to form colored products, has been widely used for the detection and colorimetric determination of nitrites. Some amines are also used in the nitrite test as coupling agents. Many of the amines used in this manner are discussed in the following sections, although many others are included in a later section on dyes.

A number of diazotized bases have been employed for the detection of ammonia in air.[9]

Many nitrogenous bases, including heterocyclic nitrogen compounds and alkaloids, have been used with potassium iodide for the detection of bismuth, with which they form red salts.

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2. A. M. Jefferson, *J. Am. Chem. Soc.* 24, 540-62 (1902).
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2-ACETAMINO-6-AMINOBENZOTHIAZOLE

Use: Detection of iridium.

2-Acetamino-6-aminobenzothiazole gives a purplish-brown precipitate with solutions of chloroiridic acid. The highly colored iridium ion itself interferes with the test if the solution is too dilute. A solution containing 0.15 mg. of iridium ion in 100 ml. of water has the same color intensity as a similar solution containing an additional 0.15 mg. of the above reagent. No definite test is obtained with less than 0.02 mg. of iridium per ml.[1]

Palladium does not interfere, but ferric iron and ruthenium must be removed before applying the test for iridium. Ruthenium is separated as follows:

Procedure. Treat the solution of ruthenium and iridium chlorides with potassium carbonate and potassium nitrite. Evaporate to dryness and cover the residue with alcohol. Ruthenium dissolves but iridium does not. Treat the residue with hydrochloric acid and add a little of the reagent.

Ferric iron is difficult to separate.

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p-AMINOACETOPHENONE

C_8H_9ON Mol. Wt. 135.16 Beil. Ref. XIV, 46.

$$CH_3—CO—C_6H_4—NH_2$$

Use: Detection and determination of palladium.

p-Aminoacetophenone is a pure white crystalline compound. It melts at 105-6° and boils at 293-5°. It is soluble in alcohol, ether, and hot water, but is only slightly soluble in cold water and benzene.

Preparation: Mix 2 parts of aniline with 5 parts of acetic anhydride and 3 parts of zinc chloride, and heat 4-5 hrs. Boil for 3-4 hours under reflux with concentrated hydrochloric acid to decompose the amide, and then mix with sufficient sodium hydroxide to redissolve the zinc hydroxide which precipitates. Separate the brown oil with a separatory funnel and remove the aniline with steam. When all aniline is over, filter, and again heat the residue with fresh water as long as anything dissolves. Collect all extracts. Concentrate by evaporation, cool, and collect the crystals.[2]

Detection of palladium. *p*-Aminoacetophenone reacts with palladium salts in neutral or weakly acid solutions to form a voluminous, yellow complex salt. This complex is insoluble in cold water, dilute acids, alcohol, ether, acetone, and chloroform. It is decomposed by strong alkalies.[1]

This reaction serves as a satisfactory method for the detection of palladium, and also for the separation of this metal from other cations, especially platinum, iridium, osmium, ruthenium and rhodium, and also from iron and gold. Only cerium salts interfere, and these must be removed before making the test.

Reagent. Dissolve 1 g. of *p*-aminoacetophenone by heating in 40 ml. of water acidified with 2 ml. of concentrated hydrochloric acid, and when the solution is cool, dilute to 100 ml.

Procedure. Dilute the solution to be tested with an equal volume of the reagent. If palladium is present, a turbidity or yellow voluminous precipitate appears. As little as 5γ $PdCl_2$ per ml. gives a positive test.

Determination of palladium. The turbidity produced when *p*-aminoacetophenone is added to very dilute solutions of palladous salts may be used for the nephelometric estimation of palladium.[1]

1. R. Schoental, *Mikrochemie.* **24**, 20-1 (1938); *C.A.* **32**, 4464 (1938).
2. J. Klingel, *Ber.* **18**, 2688 (1885).

1-AMINOANTHRAQUINONE

$C_{14}H_9O_2N$ Mol. Wt. 223.22 Beil. Ref. XIV, 177.

$$C_6H_4{=}(CO)_2{=}C_6H_3{-}NH_2$$

Use: Detection of nitrite.

1-Aminoanthraquinone is a red crystalline compound melting at 242-243° C. It is insoluble in water, but dissolves readily in alcohol, ether, benzene and glacial acetic acid. It is moderately soluble in concentrated hydrochloric acid.

Preparation: 1-Aminoanthraquinone may be prepared by the reduction of 1-nitroanthraquinone with ammonium sulfide.[1]

Detection of nitrites. 1-Aminoanthraquinone has been studied as a reagent for nitrous acid by Dubsky and Okac.[2,3] An alcoholic or acetic acid solution of the reagent may be used to detect nitrite at a concentration of 1:100,000. The test is not improved by coupling with phenol, α-naphthol or α-naphthylamine.

1. H. Roemer, *Ber.* **15**, 1790 (1882).
2. J. V. Dubsky and A. Okac, *Rec. trav. chim.* **46**, 296 (1927).
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p-AMINOBENZENEAZODIMETHYLANILINE

$C_{14}H_{16}N_4$ Mol. Wt. 240.27 Beil. Ref. XVI, 335(319).

$$H_2N{-}C_6H_4{-}N{=}N{-}C_6H_4{-}N(CH_3)_2$$

Use: Detection of nitrites and platinum.

This compound is obtained as brick-red needles from dilute alcohol. It melts at 182-183° C. It is insoluble in boiling water, but dissolves in almost all organic solvents.

Preparation: Diazotize *p*-nitroaniline and gradually mix with a well-cooled solution of 1 mole of dimethylaniline hydrochloride. Allow to stand several hours, filter, wash with cold water, dissolve in boiling, dilute hydrochloric acid, and filter. Let cool, collect the crystals which form, and then prepare the free base by treating with ammonia. Crystallize the brown powder from alcohol. Reduce the free base by warming its alcoholic solution with ammonium sulfide. The reduction is indicated by a change in color from brown to yellow. Mix with water to form a bright orange precipitate. Purify by washing, dissolve in dilute hydrochloric acid, filter, and precipitate with ammonia.[1]

Detection of nitrite. Nitrites may be detected by means of the color changes which occur when the reagent is added to a solution containing a nitrite.[2]

Reagent. Dissolve 0.5 g. of *p*-aminobenzeneazodimethylaniline in 1 liter of dilute hydrochloric acid.

Procedure. Add a few drops of the reagent and a few drops of hydrochloric acid to the solution to be tested, and then while stirring add a few drops of ammonium hydroxide. A blue color forms if nitrite is present. As little as 0.015 g. of $NaNO_2$ can be detected in one liter of solution.

Reaction with platinum. When an aqueous solution of *p*-aminobenzeneazodimethylaniline hydrochloride is added to a solution of platinum chloride, a double platinum salt separates as a brown, bulky precipitate consisting of microscopic needles. This compound has the following composition:[1]

$$[H_2N—C_6H_4—N{=}N—C_6H_4—N(CH_3)_2]\cdot 2HCl\cdot PtCl_4$$

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1. R. Meldola, *J. Chem. Soc.* 45, 107 (1884).
2. R. Meldola, *Ber.* 17, 256 (1884).

p-AMINOBIPHENYL

$C_{12}H_{11}N$ Mol. Wt. 169.20 Beil. Ref. XII, 1318.

$$C_6H_5—C_6H_4—NH_2$$

Use: Detection of sulfate.

p-Aminobiphenyl is obtained as leaves from alcohol or water. The compound melts at 53° C. and is volatile with steam. It is slightly soluble in cold water, but dissolves readily in hot water, and in alcohol, ether, and chloroform.

Preparation: Place 100 g. of carefully dried diazoaminobenzene in a 2-liter flask with 900 ml. of dry paraffin oil poured over it, and heat on a wire gauze. After the diazo compound has dissolved, raise the temperature to 150° C. Nitrogen is evolved. The reaction is completed in 2 hours. To recover the base, dilute the mixture with ether and shake with dilute hydrochloric acid until a test drawn off gives no more precipitate with sulfuric acid. Filter, and decompose the filtrate with sulfuric acid. The sulfate is insoluble.[2]

The diazoaminobenzene is prepared according to the method of Hirsch.[3]

Detection of sulfate. *p*-Aminobiphenyl reacts with sulfuric acid or solutions of sulfates containing formaldehyde to form an insoluble crystalline precipitate, which may be used for the microdetection of the sulfate ion.[1]

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1. E. Pozzi-Escot, *Rev. cienc. (Peru)*. 38, No. 418, 69-70 (1936); *C.A.* 31, 8427 (1937).
2. Fr. Heusler, *Ann.* 260, 232-3 (1890).
3. R. Hirsch, *Ber.* 25, 1973 (1892).

p-AMINODIMETHYLANILINE Synonym: Dimethyl-*p*-phenylenediamine

$C_8H_{12}N_2$ Mol. Wt. 136.19 Beil. Ref. XIII, *72.*

$$H_2N—C_6H_4—N(CH_3)_2$$

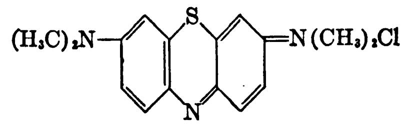
Uses: Detection of bromine, chlorine, copper, hydrogen cyanide, hydrogen sulfide, manganese and vanadium.

Determination of chlorine, hydrogen sulfide, manganese and vanadium.

p-Aminodimethylaniline is obtained as a white crystalline solid from a benzene solution on the addition of ligroin. It melts at 41° C. It is easily soluble in cold water, alcohol, benzene and chloroform, but it is less soluble in ether, and is insoluble in ligroin.

Preparation: Dissolve 200 g. of dimethylaniline in 500 g. of hydrochloric acid and dilute with water to 1 liter. Add slowly, with shaking, a well-cooled solution containing somewhat more than the calculated quantity of sodium nitrite dissolved in the least possible quantity of water. Filter off the yellow precipitate of *p*-nitrosodimethylaniline with suction. Wash with concentrated hydrochloric acid, and press the crystals between cloth. Next reduce with tin and hydrochloric acid by adding slowly the nitroso compound with moderate warming. Then heat more strongly to dissolve the tin double salt. Pour off the solution from the unreacted tin into a solution of sodium hydroxide. The free base separates as a brown oil on the surface of the warm alkali solution, and is dissolved in benzene, dried, and distilled.[1]

Detection of **hydrogen sulfide.** The thiazine dye, methylene blue, is $C_{16}H_{18}N_8ClS$,



is formed when *p*-aminodimethylaniline reacts with hydrogen sulfide and ferric chloride in a strongly acid solution. The reaction takes place according to the following equation:

$$2H_2N—C_6H_4—N(CH_3)_2 + 6FeCl_3 + H_2S \rightarrow$$
$$C_{16}H_{18}N_3ClS + NH_4Cl + 6FeCl_2 + 4HCl$$

This reaction has been used by Fischer and others[2-5] as the basis for a very sensitive method for the detection of hydrogen sulfide and soluble sulfides.

Procedure. Mix 5 ml. of the aqueous solution to be tested with 0.1 ml. of concentrated hydrochloric acid and add a crystal of *p*-aminodimethylaniline sulfate. When the solid is dissolved, add 1-2 drops of ferric chloride solution. If hydrogen sulfide is present a clear blue color is obtained.

According to Truesdale[5] this reaction is not as sensitive as the well-known alkaline lead acetate test.

Determination of hydrogen sulfide. The reaction between *p*-aminodimethylaniline, hydrogen sulfide, and ferric chloride, which results in the formation of methylene blue, is used for the colorimetric determination of hydrogen sulfide. Under properly controlled conditions, the intensity of the color developed is proportional to the amount of hydrogen sulfide present, and the color is stable for several weeks. Variations in the amounts, or in the order of addition of the reagents alter the intensity of the color. Standards must be prepared from solutions containing known amounts of hydrogen sulfide, which have been determined iodometrically, since colors produced in the reaction used in the determination are not exactly the same as those formed by the dilution of solutions of methylene blue.[6,7,20] This method has been applied to the determination of sulfur in iron,[10,21] food, tissue, water, and sewage.[9] Interference by organic matter, alkalinity, nitrites and nitrates may easily be avoided.[32] As little as 0.01 mg. of sulfide per liter can be detected by this method. The following procedure for determining hydrogen sulfide in water has been described by Yoe.[8]

Standard sulfide solution. Prepare hydrogen sulfide by the action of hydrochloric or sulfuric acid on ferrous sulfide, and wash the gas by bubbling through water. Pass the washed gas slowly for 1 or 2 minutes into 300 ml. of cool, boiled distilled water. Add an aliquot of this solution to a known excess of 0.01 N iodine solution, and titrate with 0.01 N sodium thiosulfate solution. Treat measured volumes of this solution in the same way, and at the same time as the sample.

Procedure. If the water to be analyzed contains from 1-3 mg. of hydrogen sulfide per liter, use 500 ml. of the sample, and to this add the following: 10 ml. of hydrochloric acid (sp. gr. 1.19), 0.025 g. *p*-aminodimethylaniline sulfate, and 2.5 ml. of 0.1 N ferric chloride in 6 N hydrochloric acid. Mix well and allow the mixture to stand for several hours and compare the resulting color with that of standards similarly prepared.

If the water contains less than 1 mg. of hydrogen sulfide per liter, add to 500 ml. of the sample 10 ml. hydrochloric acid (sp. gr. 1.19), 0.01 g. *p*-aminodimethylaniline sulfate, and 1 ml. of 0.1 N ferric chloride in 6 N hydrochloric acid.

Almy[9] has used the above reaction to determine hydrogen sulfide in food products. The hydrogen sulfide is removed with a current of carbon dioxide from an acidified aqueous suspension of the material to be tested, and is absorbed in a solution of zinc acetate. The hydrogen sulfide, which is precipitated as zinc sulfide, is then determined with the aid of *p*-aminodimethylaniline. This method may also be used for the determination of sulfides in feces,[33] sewage and mineral waters, and gelatine.[34] The following method is described by Almy:[9]

Reagents. *p-Aminodimethylaniline reagent:* Dissolve 0.04 g. of *p*-aminodimethylaniline hydrochloride in 100 ml. of 1:1 hydrochloric acid. This solution must be prepared fresh every 24 hours.

Ferric chloride solution: Dissolve 27 g. of ferric chloride hexahydrate in 500 ml. of concentrated hydrochloric acid and dilute to 1 liter. Dilute with 4 volumes of distilled water just before use.

Zinc acetate solution. Add a slight excess of a thick aqueous suspension of zinc oxide to 135 g. of glacial acetic acid and dilute to 1 liter. This solution contains about 20 per cent zinc acetate. Before use, filter to remove suspended material, and dilute 10 ml. of the clear filtrate to 100 ml. to obtain a 2 per cent solution, or 3 ml. to 100 ml. for a 0.6 per cent solution.

Standard sulfide solutions. Pass washed hydrogen sulfide slowly for 1-2 minutes into 300 ml. of cool, boiled distilled water. Add an aliquot of this solution to a measured excess of 0.01 N iodine solution and titrate with 0.01 N sodium thiosulfate solution.

From the titration, determine the quantity of the above solution which, on dilution to 500 ml., will contain 0.01 mg. of hydrogen sulfide per ml. Place in a 500-ml. volumetric flask about 435 ml. of water, 15 ml. of 2 per cent zinc acetate solution, and the necessary quantity of hydrogen sulfide solution as calculated from the titration. Dilute to the mark, and use immediately for the preparation of the standards.

Transfer 75 ml. of 2 per cent zinc acetate solution to each of fifteen 500-ml. volumetric flasks, and then add from 315 to 375 ml. of cool, recently boiled water. To these flasks add 1, 2, 3, 4, 5, 7, 10, 12.5, 15, 20, 25, 30, 40, 50 and 60-ml. portions of the standard sulfide solution. Immediately add 25 ml. of the *p*-aminodimethylaniline solution and 5 ml. of 0.02 M ferric chloride solution. The volume in each flask should be about 450 ml. before addition of the reagent. The temperature of the solutions in the flasks should be uniform, and should not vary more than 0.5° C. from that adopted for the sample solution. Agitate gently after the addition of each reagent. Allow to stand 2 hours and dilute to 500 ml. These standard solutions are stable about 4 to 5 weeks if stored in a cool, dark place.

Procedure. Fit a tall cylinder with a three-hole rubber stopper. In one hole place a delivery tube for carbon dioxide. Connect this tube to a manometer filled with a zinc chloride solution of sp. gr. 2.0. The pressure registered is one-half that if water were used. In the second hole, place a dropping funnel containing 50 ml. of 1:1 hydrochloric acid. Fit an exit tube for hydrogen sulfide into the third hole. This tube extends below the surface of 30 ml. of 0.6 per cent zinc acetate solution contained in a 100-ml. distilling flask, which is used as an absorption vessel for the hydrogen sulfide. Connect the side arm of this flask to a tube which extends below the surface of 20 ml. of 0.6 per cent zinc acetate solution contained in a 100-ml. volumetric flask. Rubber fittings must be cleaned to remove sulfur and sulfides.

Place 50 ml. of distilled water in the cylinder, and add the sample. The size of the sample is determined by its sulfide content. Add a few drops of diphenyl ether to prevent foaming. Pass carbon dioxide through the apparatus to remove all air, and then add nearly all the acid from the dropping funnel. Continue to pass carbon dioxide through the apparatus for 15 minutes at a pressure of about 40 mm. of water.

Disconnect the two receiving vessels, and transfer the solution from the distilling flask to the volumetric flask. The total volume of the solution and washings should be about 90 ml. If the solution is turbid, the sulfide concentration is probably greater than that of the highest standard. Should this occur, dilute the sample to 100 ml., mix well, and use a suitable aliquot. In most cases 25 ml. will be suitable. Add this to 15 ml. of a 2 per cent solution of zinc acetate contained in another 100-ml. volumetric flask, and dilute to about 90 ml.

To the entire sample, or to an aliquot as described above, add 5 ml. of the freshly prepared *p*-aminodimethylaniline reagent. Mix thoroughly and add 1 ml of 0.02 M ferric chloride solution. Allow to stand 2 hours, and dilute to 100 ml. Compare the solution in a colorimeter with the standard which it most closely resembles in color.

Lindsay [10] has used the Fischer reaction for the colorimetric determination of sulfur in pig iron. The sulfur is evolved as hydrogen sulfide and is absorbed in an aqueous solution of sodium hydroxide. This solution is diluted, a portion acidified, and then treated with *p*-aminodimethylaniline, hydrochloric acid, and ferric chloride. The resulting blue color is matched in the usual manner with the color obtained by treating standard solutions of sodium sulfide similarly.

Suslova [22] has used *p*-aminodimethylanaline in a procedure for the photocolorimetric determination of small quantities of hydrogen sulfide and sulfides without the use of standard solutions. This method is based on the principle of absolute colorimetry.

Determination of vanadium. Minute quantities of vanadium may be detected colorimetrically by a method which is based upon the reaction of vanadates with *p*-aminodimethylaniline hydrochloride or sulfate, which results in the formation of Wurster red. This method has been used by Chervyakov and Ostroumov [11] for the determination of vanadium in uranium salts.

Procedure. Dissolve 0.2-0.5 g. of uranyl chloride or sulfate (nitrates and acetates must be converted to the chloride or sulfate) in 10 ml. of water, and 5-6 drops of 50 per cent hydrochloric acid. Add 0.5 ml. of phosphoric acid, 40 ml. or more of alcohol, 3-4 ml. of glycerol, and mix well. Dissolve any turbidity which forms with least possible quantity of hydrochloric acid, and add 1 ml. of 0.5 per cent *p*-aminodimethylaniline hydrochloride or sulfate solution, and compare the resulting color with that obtained in a solution prepared in the same manner, using chemically pure uranyl chloride and adding a titrated solution of a pure vanadate until the two colors match.

The color obtained in the reaction between vanadates and *p*-aminodimethylaniline is fugitive in water, but is stabilized in the presence of a large excess of alcohol. Iron salts give a similar color reaction, and are converted into complex compounds with glycerol and phosphoric acid.

Vanadium may be determined in the presence of uranium with an accuracy of 0.01 mg. of V_2O_5 when 0.16 mg. is present.

Detection of copper. A violet precipitate is obtained when a mixture of *p*-aminodimethylaniline and potassium iodide is added to a solution containing cupric ions. Free iodine is formed by the action of the cupric salts on potassium iodide, and free iodine (and other oxidizing agents), dissolve in the reagent solution with the formation of a violet color. This reaction constitutes a very sensitive test for cupric salts. As little as 1 part of copper in 2 million parts of water gives this reaction. Lead salts give a weak turbidity and bismuth salts a yellow-orange precipitate.[12]

Detection and determination of the halogens. A 5 per cent alcoholic solution of *p*-aminodimethylaniline reacts with bromine, iodine, and chlorine to give sensitive color reactions. The colors obtained are pink, red, purple, violet-red, green, brown or yellow. Bromine gives the most sensitive reaction and chlorine the least sensitive.[13]

Detection of bromine. The above reaction has been used by Jolles [15] for the detection of bromine in urine. Filter paper which has been impregnated with a 0.1 per cent solution of *p*-aminodimethylaniline in water and allowed to dry is used for this test. When bromine comes in contact with the reagent paper, a colored ring forms which is violet at the center and blue to gray-brown toward the margin. The red-violet color is more apparent when the paper is moistened.

Bromine is detected in urine by the following procedure: [15,26,27,31]

Procedure. Acidify 10 ml. of urine in a flask with sulfuric acid, and add potassium permanganate solution until a permanent pink color appears. Place a strip of filter paper, which has been saturated with a 0.1 per cent *p*-aminodimethylaniline solution, in the mouth of the flask, and expell the bromine from the solution by warming. If bromine is present, the above-described color reaction is obtained. As little as 0.001 per cent sodium bromide gives this reaction.

Detection of chlorine. A purple hue develops when *p*-aminodimethylaniline is added to a solution containing chlorine. This color appears to be due to the formation of a meriquinone compound known as Wurster's red, which is obtained as a result of the oxidation of the reagent by chlorine. The appearance of this color may be used as a sensitive test for free chlorine in water.[16]

Procedure. To 100 ml. of water, add a few drops of acetic acid, 1-2 ml. of 2 N sodium acetate, and 10 drops of 0.1 per cent *p*-aminodimethylaniline. A red to purple color indicates the presence of free chlorine. By this reaction as little as 0.03 mg. of free chlorine can be detected in 1 liter of water.

Determination of chlorine. Alfthan,[17,18] Kolthoff,[16] and others [28-30] have used the color reaction between chlorine and *p*-aminodimethylaniline for the colorimetric determination of free chlorine. The method is rapid and sensitive; and only one solution, prepared from methyl red, is needed for the colorimetric comparison. The reaction is sensitive to iron in concentrations greater than 0.1 mg. per liter. It is important that the pH of the solution in which the determination is made be maintained between 2.6 and 3.4. Further, while the reaction is extremely sensitive, it is not satisfactory for high concentrations of chlorine, or for solutions which are colored with humic acids.

Procedure. To 50 ml. of the solution to be analyzed, add 1 ml. of 50 per cent acetic acid and 2 ml. of 2 N sodium acetate solution. Add 10 drops of a 0.1 per cent alcoholic solution of *p*-aminodimethylaniline and dilute to 100 ml. Allow to stand 10-15 minutes for the color to develop, and compare with standards within the next 15 minutes.

Since iodine and chlorine solutions of the same molar concentration yield the same color intensity, a chlorine solution of unknown concentration may be compared with a standard iodine solution. This is prepared as follows:

Iodine standard. Prepare a standard iodine solution containing 0.1269 g. per liter. This solution is equivalent to 0.03546 mg. of chlorine per ml. Dilute 10 ml. of this solution to 50 ml. at the same time the sample is prepared, and compare by dilution.

A standard solution prepared from methyl red has been proposed by Alfthan.[17]

Methyl red standard. Dissolve 0.115 g. of methyl red in sufficient 0.01 N hydrochloric acid to make 1 liter of solution. One ml. of this solution is equivalent to 0.02 mg. of chlorine for a 50-ml. sample. Compare the sample with the standard by duplication.

As little as 0.01 mg. of chlorine per liter can be determined by this method.

In a thorough study of the above method for determining free chlorine, Beyers and Mellon [14] found that the optimum pH range for determining chlorine in concentrations ranging up to 0.6 p.p.m. is 2.6 to 3.4, and for higher concentrations 3.2-4.5. The optimum color development for concentrations of chlorine up to 1.6 p.p.m. were obtained with 0.4 ml. of reagent. The color is stable only for about 5 minutes, and Beer's law is valid only for chlorine concentrations up to 0.65 p.p.m. The following procedure is recommended:

Reagent. Dissolve 0.10 g. of *p*-aminodimethylaniline hydrochloride in 10 ml. of water to which are added 25 ml. of 85 per cent phosphoric acid, and 15 ml. of water containing 1 g. of iron-free sodium dihydrogen phosphate dodecahydrate. This solution is stable for 6 weeks.

Procedure. Add 0.4 ml. of the above reagent to 100 ml. of the sample to be analyzed, and compare the resulting color with that obtained by diluting to 100 ml. the required volumes of acidified methyl red solution prepared according to the directions of Alfthan and Jarvis.[18]

The methyl red standard is prepared as follows: Dissolve 0.115 g. of methyl red in 5 ml. of 1 N sodium hydroxide solution, and dilute to 100 ml. with water containing 5 ml. of 0.01 N sodium thiosulfate solution. Dilute 10 ml. of this solution to 1 liter. This gives a 0.00115 per cent solution of methyl red. One ml. of this solution acidified with a few drops of hydrochloric acid corresponds in color to that developed with 100 ml. of water containing 0.1 mg. of chlorine per liter.

According to Hasse and Gad,[25] the use of phosphoric acid in the preparation of the reagents eliminates some of the difficulties encountered in the use of *o*-tolidine.

The use of *p*-aminodimethylaniline seems to offer no advantages over the *o*-tolidine method except that perhaps some operators may prefer to match purple rather than yellow hues.

Detection and determination of manganese. Schmidt[23] has used *p*-aminodimethylaniline for the detection and determination of small quantities of manganese, especially in water. This test depends on the formation of a reddish-violet color when the reagent is added to a solution containing manganese salts.[24]

Procedure. Acidify 100 ml. of water with 3 ml. of 3 N hydrochloric acid, and then remove any carbon dioxide by drawing air through the mixture. Make alkaline with sodium hydroxide, again draw air through the mixture, and add 2 drops of a 2 per cent aqueous solution of *p*-aminodimethylaniline. Add a 10 per cent solution of citric acid dropwise until a color appears, and then add 3 drops in excess. As little as 0.04 mg. of manganese may be detected in 1 liter by this method.

Manganese can be determined colorimetrically by means of the above procedure by comparing the color formed with that of standards similarly prepared.

Ferric salts and nitrites interfere with this reaction. Interference due to iron may be eliminated by the formation of the ferric complex with citric acid. Nitrites are destroyed by adding 2 drops of 5 per cent sodium azide to the solution to be analyzed. Magnesium, when present in concentrations greater than 50 mg. per liter, also interferes. The time required for the analysis is about 15 minutes.

Detection of hydrogen cyanide. *p*-Aminodimethylaniline may be substituted for guaiac in the reaction of Pagenstecher and Schoenbein for the detection of hydrogen cyanide. This test consists in dipping filter paper into a solution of the reagent, drying, moistening with a solution of copper sulfate, and then suspending in a bottle of the gas suspected of containing hydrogen cyanide. In the presence of this gas the paper turns a Burgundy-red.[19]

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2-AMINOETHANOL

Synonym: Monoethanolamine

C_2H_7ON Mol. Wt. 61.08 Beil. Ref. IV, *274*.

$$HO—CH_2—CH_2—NH_2$$

Use: Determination of mercury. Detection of copper.

2-Aminoethanol is a colorless, viscous, oily liquid which possesses a faint odor. Its sp. gr. is 1.022, boiling point 171-2°, melting point 10.5°, and flash point 93° C. The refractive index is 1.4539. The compound is miscible with water and alcohol. It is also soluble in chloroform and carbon tetrachloride, but only slightly soluble in benzene.

Preparation. 2-Aminoethanol is prepared by heating 2-chloroethanol with aqueous ammonia in a closed tube.[2]

Determination of mercury. Meltsner, Wohlberg, and Kleiner[3] observed that 2-aminoethanol reduces mercury salts in an aqueous solution, and suggested that it might be used successfully for the quantitative determination of mercury. The following method has been suggested by Rauscher[1,5] for the determination of mercury in organic and inorganic compounds:

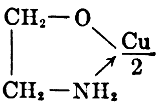
Procedure. Reflux the weighed sample with 2-aminoethanol for 5 minutes and allow to cool. Dilute with water, remove the supernatant liquid, and collect the mercury into a single globule. Wash with water and dry methyl alcohol. Weigh the mercury, or dissolve it in nitric acid and titrate with standard thiocyanate.

Samples containing quantities of mercury ranging from 3 to 370 mg. have been analyzed successfully.

Reaction with copper. The ethanolamines react with salts of copper to yield crystalline compounds of the type, $[Cu(ethanolamine)_m]X$. The value of m is 3 for monoethanolamine when X is the sulfate ion, or

$$[Cu(HO-CH_2-CH_2-NH_2)_3]SO_4$$

It appears that the functional groups, NH_2 and OH, form chelate rings with copper as the central ion. Thus,



Hot concentrated solutions of the ethanolamines reduce cupric to cuprous ions and to the metal, and they also form amorphous organic copper compounds of variable composition.[4]

1. Wm. H. Rauscher, *Ind. Eng. Chem., Anal. Ed.* 10, 331-3 (1938); *C.A.* 32, 6174 (1938).
2. A. Wurtz, *Ann.* 121, 228 (1862).
3. M. Meltsner, C. Wohlberg, and M. J. Kleiner, *J. Am. Chem. Soc.* 57, 2554 (1935).
4. J. W. Cole and M. B. Shreaves, *Va. J. Sci.* 3, 27 (1942).
5. Wm. H. Rauscher, *Ind. Eng. Chem., Anal. Ed.* 9, 296 (1937).

4-AMINO-3-METHYLPHENYLMORPHOLINE

$C_{11}H_{16}ON_2$ Mol. Wt. 192.24

$$O=(CH_2-CH_2)_2=N-C_6H_3(CH_3)-NH_2$$

Use: Detection of gold.

4-Amino-3-methylphenylmorpholine is only slightly soluble in water, but dissolves readily in acetone, alcohol and alcohol-water mixtures to give deep reddish-brown colored solutions.

Detection of gold. 4-Amino-3-methylphenylmorpholine reacts with solutions of gold salts to yield a pink color. This reaction is sensitive to 1 part of gold in 30,000,000 parts of solution. The reagent also gives a pink color with chromium, vanadium, osmium, and europium; a purple color with copper and ferric iron; a brown precipitate with platinum; and a purple precipitate with silver. Silver reacts only in neutral solutions, but other ions react most satisfactorily at pH 3-5. The reagent used is a 0.2 per cent solution of the organic compound in 50 per cent alcohol. The reaction with gold is best obtained at a pH of 2.5-3.0; above pH 7 results are not satisfactory. The pink color obtained in the reaction of gold appears to be fairly stable when formed in a solution of gold at a concentration of 1 p.p.m.[1,2]

1. W. J. Frierson and P. M. Simpson, *Va. J. Sci.* 3, 11 (1942); *C.A.* 36, 3113 (1942).
2. W. J. Frierson, *Va. J. Sci.* 3, 279 (1943).

α-AMINOPYRIDINE

$C_5H_6N_2$ Mol. Wt. 94.11 Beil. Ref. XXII, 428.

$$C_5H_4N{-}NH_2$$

Use: Detection of antimony, bismuth, cobalt, copper, gold and zinc.

α-Aminopyridine consists of white leaflets or large colorless crystals. The compound melts at about 55° and boils at 203-5°. It is soluble in water, alcohol, benzene, and ether.

Preparation: Grind 10 g. of sodamide under xylene in a mortar and add to 16 g. of pyridine which has been dried over potassium hydroxide or barium oxide, distilled, and mixed with 30 ml. of sodium-dried xylene. Heat the mixture under reflux in an oil bath to 140-50° for 7 hours. Carry out under anhydrous conditions. Cool, and add gradually and cautiously 20 ml. of cooled sodium carbonate solution. Shake well and separate the two layers. Extract the aqueous layer several times with benzene. Then combine the extracts and dry over solid potassium hydroxide, and finally distill off the solvent. Purify by vacuum distillation. α-Aminopyridine boils at 93°/11 mm. and at 96°/13 mm. The product is recrystallized from ligroin.[1,2]

Microchemical reactions. α-Aminopyridine and ammonium thiocyanate form characteristic crystals with cobalt, copper, and zinc.[3] Bismuth, antimony, and gold may be detected by a somewhat different procedure.[4]

Procedure. To a drop of the acid solution to be tested add (in testing for gold) a small crystal of sodium bromide or (in testing for bismuth and antimony) a small crystal of potassium iodide, and then add a little of the reagent.

Bismuth yields a characteristic scarlet precipitate, and antimony an orange-yellow precipitate. The crystals of the antimony compound are larger than those of bismuth. As little as 0.0012 mg. of antimony and 0.0075 mg. of bismuth may be detected. Gold yields yellow-red rectangular lamellas and H-formed crystals. In the presence of silver, lead, mercury, copper, cadmium, tin. or gold, bismuth is first separated by means of sodium hydroxide and potassium cyanide.

1. A. Tschitschibabin, *Chem. Zentr.* I, 1065 (1915).
2. J. P. Wibaut, *Rec. trav. chim.* 42, 240 (1923).
3. A. Sá, *Anales farm. bioquim. (Buenos Aires)*. 4, 77-80 (1933); *C.A.* 28, 3027 (1934).
4. A. Sá, *Anales farm. bioquim. (Buenos Aires)*. 5, 3-7 (1934); *C.A.* 30, 2876 (1936).

ANILINE

Synonym: Aminobenzene, phenylamine

C_6H_7N Mol. Wt. 93.12 Beil. Ref. XII, 59.

$$C_6H_5—NH_2$$

Uses: Detection of aluminum, ammonia, bismuth, bromine, cadmium, chlorate, chlorine, chromium, cobalt, copper, gold, hydrogen cyanide, hydrogen peroxide, iodide, iridium, iron, lead, mercury, molybdenum, nickel, nitrate, nitrite, osmium, palladium, perborate, percarbonate, persulfate, platinum, potassium, rhenium, ruthenium, sodium, tin, tungsten, vanadium and zinc.

Determination of aluminum, cerium, chlorate, chromium, hydrogen peroxide, iron, lead, potassium, sodium, thorium, titanium, tungsten, water and zirconium.

Aniline is a colorless liquid. It is colorless when freshly distilled but darkens on exposure to light and air. It has a characteristic odor and a burning taste. It boils at 183° C. and has a sp. gr. of 1.022. One gram of the liquid dissolves in 28.6 ml. of cold water and 15.7 ml. of boiling water. It is miscible with alcohol, benzene, chloroform and many other organic solvents. It reacts neutral to litmus but exhibits decided basic properties.

Precipitation of metals. Aniline reacts with aqueous solutions of various metallic salts to yield precipitates of the metallic hydroxides. Allen[1] reports that titanium, aluminum, chromium, zirconium, cerium, thorium and ferric iron are quantitatively precipitated with aniline, while magnesium, calcium, strontium, manganese and ferrous iron are not precipitated. Jefferson[2] has used aniline for the precipitation of thorium and cerium, and states that the method may be used for the separation of thorium from lanthanum and praseodymium, and zirconium from lanthanum. Kolb[3] and Justel[4] have also studied the precipitation of thorium with aniline.

Kozu[5,6] has recommended the precipitation of aluminum from potassium alum by the addition of a saturated aqueous solution of aniline. The reaction is complete at pH of 4.45-4.50. The precipitate is compact and easily filtered and washed. Aluminum may be separated from manganese, nickel, cobalt and zinc by this method.

Schoeller and Schrauth[7] precipitate chromium in the presence of manganese by the following procedure:

Procedure. Heat to boiling 300 ml. of a neutral solution containing 0.1-0.2 g. of chromium and add 1 ml. of aniline. Boil for 5 minutes and allow the mixture to stand for 5 minutes on a water-bath. Filter, wash, and ignite to Cr_2O_3.

This method is satisfactory for the separation of chromium from manganese.

Detection of mercury and tin. An excess of mercuric chloride reacts with stannous chloride in an acid solution to give mercurous chloride and stannic chloride:

$$2HgCl_2 + SnCl_2 \rightarrow 2HgCl + SnCl_4$$

This reaction is used for the detection of mercury or tin. This test, however, is not very sensitive due to the difficulty in observing small quantities of the white mercurous chloride. If this reaction is carried out in an alkaline solution, mercuric chloride is reduced to metallic mercury, which separates as an easily perceptible black precipitate. The proper alkalinity for this reaction may be obtained by the use of alkali hydroxides, ammonia or aniline. Aniline is recommended, however, since its alkalinity is so small that the presence of trivalent antimony, which may reduce mercuric chloride to mercury in the presence of stronger alkalies, does not interfere. Mercury is detected by a spot test devised by Tananaev: [8-11]

Procedure. Place a drop of the solution to be tested on a strip of filter paper and treat with a drop of freshly prepared stannous chloride solution and a drop of aniline. A gray to black color indicates the presence of mercury. This test is sensitive to about 1γ of mercury at a concentration of 1:50,000.

Large quantities of silver may also yield a gray spot, but may be removed with potassium chloride. The following procedure may also be used if much silver is present.

Procedure. Place a drop of the solution to be tested on a strip of filter paper and add a drop of potassium thiocyanate and a drop of stannous chloride, and then treat with a drop of aniline. A greenish ring and a black ring may be formed although the green ring disappears on the addition of ammonium hydroxide, while the black ring remains unchanged.

Davies [12] has used this reaction for the detection of mercury in a systematic scheme of analysis. Mercuric sulfide, obtained in the usual manner, is dissolved in bromine water, and the resulting solution treated with stannous chloride and aniline.

Tin is detected by a similar reaction in which mercuric chloride and aniline are used as the reagent.

Procedure. Impregnate a strip of filter paper with a solution of mercuric chloride and allow to dry. Place a drop of the solution containing stannous tin on the paper and add a drop of aniline. The test solution should be neutral or only very slightly acid. A brown to black spot is formed if tin is present. By this reaction 0.6γ of tin can be detected at a concentration of 1:83,000.

If tin is present as stannic salts it must first be reduced. This is most conveniently effected by mixing a drop of the solution to be tested on a watch glass with a drop of concentrated hydrochloric acid and a small piece of metallic magnesium. Apply the test to a drop of the reduced solution.

Detection of bismuth. Like many other organic bases, aniline reacts with bismuth salts to form an insoluble, colored double iodide. This reaction may be used for the detection of bismuth.

Procedure. To make the test, dissolve bismuth hydroxide in nitric acid, evaporate to dryness, and redissolve the residue in water. Add a drop of this solution to a solution of potassium iodide, stannous chloride and aniline on a watch glass. With bismuth, a yellow to red color is obtained which is not destroyed by potassium thiocyanate.[13]

Detection of cobalt, copper, nickel, cadmium, zinc, iron and aluminum. Various metals react with ammonium or potassium thiocyanate in the presence of aniline to yield characteristic crystals which are used for the detection of these metals.[14,15,17,21] Ammoniacal solutions of copper, nickel and cadmium salts yield with ammonium thiocyanate and aniline crystalline compounds of the type $[(C_6H_5—NH_2 \cdot HCNS)_2M(NH_3)_4](CNS)_2$. These compounds have the following colors: copper, green; nickel, pale green; cadmium, colorless; and cobalt gives a rose-colored precipitate. Dubsky[15] reports that cobalt yields a lilac colored compound, $[Co(C_6H_5NH_2)_2(CNS)_2]$; and in a strongly ammoniacal solution copper yields $[Cu(C_6H_5NH_2)_2(CNS)_2]$. The nickel compound is $[Ni(C_6H_5NH_2)_2(NH_3)_2](CNS)_2$. Cadmium forms $[Cd(C_6H_5NH_2)_2(CNS)_2]$.

Martini[10] reports that zinc sulfate reacts with a dilute solution of aniline hydrochloride to yield colorless triclinic crystals of zinc aniline chloride, $C_6H_5NH_2 \cdot HCl \cdot ZnCl_2$.

Korenman[20] prepares a clear reagent which is stable for many days by mixing equal parts of water and aniline, then making the mixture permanently acid by shaking with dilute hydrochloric acid, and finally saturating with ammonium thiocyanate. A drop of this reagent when mixed with a drop of solution containing copper or cadmium yields characteristic crystals which may be identified microscopically. Dwyer and Murphy[18] recommend a reagent prepared as follows:

Reagent. Shake 20 ml. of 5 per cent ammonium thiocyanate solution with 18.6 g. of aniline to form an emulsion. Add 5 N hydrochloric acid until the emulsion clears, and then add an additional 3-4 drops of aniline and sufficient water to make 100 ml. of solution. Clear the mixture by adding a little ethyl alcohol. No cloudiness should result when 1-3 drops of this reagent is added to 5 ml. of water. This reagent is stable for several months if stored in a dark bottle and protected from oxidation.

Procedure. Treat 5 ml. of solution to be tested with 3-4 drops of the reagent. A yellowish-brown precipitate or coloration appears within 2 minutes if 1γ of copper is present.

Silver, lead, mercury, bismuth, chromium, aluminum, cadmium, zinc, cobalt, nickel and manganese interfere and must be removed before making the test.

When a solution of pyrocatechol in acetic acid is added to a solution containing ferric iron, an amorphous violet precipitate is formed. Upon treating with aniline, cubic crystals and finally violet platelets are formed. This reaction will detect 0.2γ of iron. Under similar conditions 1γ of aluminum gives star-shaped clusters. Chromium does not react.[21] Cadmium may be detected with the aid of a mixture of aniline and an alkali iodide. The cadmium compound crystallizes as an insoluble substance which may easily be recognized.[16]

Detection of the platinum metals. Whitmore and Schneider[22] have investigated the use of aniline hydrochloride as a microchemical reagent for the platinum metals. The test is carried out by adding a small fragment of aniline hydrochloride to a little of the aqueous solution to be tested. The results are given in Table 33, which is taken from the work of Whitmore and Schneider:[22]

TABLE 33.—REACTION OF THE PLATINUM METALS WITH ANILINE HYDROCHLORIDE

Salt	Reaction
$RuCl_3$	A very scant, green, amorphous precipitate forms after standing some time.
$RhCl_3$	No apparent reaction.
$PdCl_2$	A dense, yellow precipitate forms which consists of many small branching structures. Near the edge of the drop some bright yellow, rectangular prisms appear.
Na_2OsCl_6	A great many small radiating clusters of bright-yellow prisms appear gradually. On standing many bright-yellow hexagonal plates appear near the edge of the drop. Many of these resemble small rectangular prisms.
$IrCl_4$	A dense, green, amorphous precipitate is formed immediately. Throughout this precipitate a great many small, hexagonal plates appear. These occur singly and a few in radiating clusters.
H_2PtCl_6	A dense, pale yellow precipitate forms immediately around the test particle. Throughout this precipitate many, light yellow, rectangular prisms develop. Many of these occur in groups in which the individual prisms are arranged parallel to each other.
$AuCl_3$	A green, amorphous precipitate forms immediately around the test particle.

Detection of rhenium. Rhenium chloride dissolves in hydrochloric acid to form chlororhenic acid, $HReCl_4$. This substance reacts with aniline to give a crystalline compound which is used for the microdetection of rhenium. A characteristic crystalline compound is also formed with H_2ReCl_6.[23]

Detection of iodide. Iodide may be detected in the presence of bromide and chloride by a test devised by Korenman.[24]

Procedure. Mix a drop of the solution to be tested with a drop of 1:4 or 1:5 mixture of aniline and sulfuric acid and 2-3 crystals of potassium dichromate. Crystals which are easily observed under a microscope are formed if iodides are present. These crystals consist of the periodide, $6C_6H_5NH_2 \cdot 3H_2SO_4 \cdot HI \cdot I_4$. The sensitivity of this reaction is 1:9000. Bromides and chlorides in quantities of 275 and 660 times respectively that of the iodide do not interfere.

Detection and determination of sodium and potassium. Aniline perchlorate has been used as a substitute for perchloric acid as a precipitant for potassium. According to Hill,[25] the preparation of aniline perchlorate by evaporation of ammonium perchlorate with aniline is not satisfactory, since the decomposition is slow and the product dark colored. He recommends adding aniline in slight excess to an aqueous solution of perchloric acid and boiling to remove the excess aniline.

Kuzirian[26] recommends the following procedure:

Procedure. Dissolve the mixed chlorides in water, and for each 1.5 ml. of water, add 50 ml. of absolute alcohol (99.5 per cent). Then add dropwise with shaking a weighed quantity of aniline perchlorate dissolved in 50 ml. of absolute alcohol. Allow the mixture to stand for 1 hour and filter off the precipitate of potassium perchlorate.

Aniline bitartrate in 50 per cent alcohol is also used for the separation and determination of potassium.[27] For the separation of sodium and potassium, proceed as follows:

Reagent. Dissolve 9.3 g. of pure aniline and 15 g. of tartaric acid in 1 liter of a mixture consisting of equal volumes of alcohol and water.

Procedure. To the solution containing the potassium and sodium salts, add 9 times its volume of 1:1 alcohol and 4 volumes of aniline bitartrate solution. Allow to stand 15 minutes, filter and wash the precipitate of potassium bitartrate with 1:1 alcohol. This reaction is sensitive to 0.0004 N potassium chloride solution. Sodium is not precipitated.

For the determination of potassium, use a reagent similar to that described above by preparing in a mixture consisting of 1 part water and 4 parts by volume of alcohol.

Procedure. Dissolve 0.15-0.4 g. of the salts in 12.5 times as much water and 50 times as much 95 per cent alcohol. Then add 120-200 per cent of theory of aniline bitartrate in the 4:5 alcohol solution. Allow to stand overnight and filter off the potassium salt. Wash with 4:5 alcohol, dry, ash the filter paper, treat with 10 drops of concentrated hydrochloric acid and again evaporate to dryness. Ignite gently, cool, add a little ammonium nitrate and a few drops of water and again ignite. Weigh as potassium chloride.

Lutz[28] has used a saturated solution of aniline silicofluoride for the detection of potassium. The addition of alcohol causes a better separation of the precipitate. The test is carried out by adding one ml. of a saturated solution of the reagent to 5 ml. of the solution to be tested. The test is sensitive to one part of potassium in 1022 parts of solution.

Detection of chlorate. A number of oxidizing agents are capable of converting aniline to a blue oxidation product. This reaction has been used for the detection and the determination of a number of different substances. Among the oldest and the best known of these reactions is that between aniline and chlorates, which has been widely used for the detection[29-35] and the colorimetric determination of the chlorate ion.[35-38] The test may be carried out as follows:

Procedure. To a little of the solution to be tested in a test tube, add a little aniline sulfate and then allow 3-4 ml. of concentrated sulfuric acid to run down the side of the tube. A blue color appears at the junction of the two liquids. This test will detect 0.05 mg. of potassium chlorate in 1 ml. of solution. Under the same conditions nitrates and iodates give a brownish-red color.

Pieraerts [29] recommends the use of an ethyl alcohol solution of aniline. This reagent consists of 20 ml. of freshly distilled aniline, 100 ml. of 94 per cent ethyl alcohol and sufficient water to make 200 ml. of solution.

The blue color formed in the aniline-chlorate reaction can be extracted with chloroform, ether or amyl alcohol.[29]

Lesnicenko [32] has modified the aniline reagent for chlorate by adding silver nitrate. The presence of silver causes an acceleration of the reaction and intensifies the color shade. A qualitative reagent is prepared by dissolving 50 mg. of silver nitrate in 100 ml. of hydrochloric acid ($d = 1.19$) and 5 g. of aniline. In the presence of 0.1-0.0001 per cent potassium chlorate, the characteristic color change is violet, blue and green. The maximum color intensity develops in about 30 seconds and the color disappears in 10-30 minutes. In the presence of 5-20 per cent of sodium, potassium or ammonium nitrate, a green color appears only after 3 minutes and this persists for about 30 minutes. The color change due to chlorate is observed before the green color of the nitrate forms.

Determination of chlorate. Chlorates are determined by means of the blue coloration produced by adding a solution of aniline hydrochloride in hydrochloric acid to a solution containing chlorate:

Reagents. *Solution A.* Dissolve 50 g. of pure aniline hydrochloride in 1 liter of 1:2 hydrochloric acid. This solution should be colorless.

Solution B. Dissolve 50 g. of pure aniline hydrochloride in 1 liter of 1:3 hydrochloric acid.

Procedure. Use 5 ml. of the sample for the analysis. If the sample contains between 0.5 and 7.0 mg. of chlorate per 5 ml., add 20 ml. of Solution A. If the unknown contains between 0.1 and 2.0 mg. of chlorate in 5 ml., add 20 ml. of Solution B. If the concentration of the unknown does not fall within the limits prescribed dilute or concentrate as necessary. A violet color develops immediately, but this soon changes to blue. If Solution A was used, allow the mixture to stand for 25 minutes, or if Solution B was used allow to stand for 15 minutes. Then compare the resulting color with a series of standards prepared similarly and simultaneously.

A number of oxidizing agents interfere. These include chlorine, hypochlorite, hypobromite, bromate, iodate, hydrogen peroxide, chromate, dichromate, manganate, permanganate, vanadate, ferricyanide, and peroxides of sodium, barium, manganese and lead. Many reducing substances also interfere. These include nitrite, chloride, citrate, tartrate, ferrous salts, arsenite, sulfite, and many organic compounds. Carbon, sulfur, phosphates, perchlorates, ferric chloride, nitrates and small amounts of nitrites do not interfere.[35]

According to Jones,[38] certain samples of aniline do not react properly with chlorates, but yield colors which fade within a few seconds. This condition is not improved by redistillation or chemical purification. Jones,[38] however, prepared a suitable reagent by the following method:

Procedure. Convert freshly distilled aniline to the hydrochloride in the usual manner and dilute within 2 ml. of the final volume. Add 2 drops of concentrated potassium chlorate solution and dilute to the proper volume required for the reagent. Allow to stand for 18 hours, filter off any precipitate which forms, and use the filtrate for the analytical reagent.

Lesnicenko [32] has prepared a quantitative reagent for chlorates by adding silver nitrate or silver sulfate to the aniline hydrochloride solution.

Reagent. Mix 0.05 g. of silver nitrate or sulfate with 100 ml. of hydrochloric acid and 5 g. of aniline.

Procedure. Mix 6 ml. of the reagent with 2 ml. of the standard and unknown solution. If the concentration of the potassium chlorate is below 0.001 per cent, use 4 ml. of the reagent. Compare the resulting color with that of standards containing known quantities of potassium chlorate.

The color forms slowly but is stable and intense. Nitrates do not yield a color with this reagent. Iodates and bromates yield the same color as chlorates. In concentrations below 0.005 per cent, iodates do no harm Bromates form a color immediately, but this disappears within a few minutes. The color due to chlorates persists.

Detection of nitrate. Aniline is used to detect nitrate as follows: [39-41]

Procedure. Mix 1 ml. of concentrated sulfuric acid with several drops of a solution prepared by dissolving 10 drops of aniline in 50 ml. of 1:6 sulfuric acid. Immerse in this solution a glass rod which has been moistened with the solution to be tested and blow across the surface of the mixture. If nitrate is present, intensely colored red streaks appear and the entire mixture gradually turns a carmine-red.

This test has been modified by Longi [42] who uses a mixture of *p*-toluidine and aniline. The sensitiveness of this reaction is 1 part of potassium nitrate in 32,000 parts of water. Chlorate, bromate, iodate, chromate and permanganate yield an intense blue color. Nitrite produces a yellow color. According to Eitel [43] aniline is one of the least sensitive of the various reagents that have been used for the detection of nitrates.

Detection and determination of lead. Lead may be detected or determined by a procedure which is based upon the oxidizing action of lead peroxide. Morgan [44] has used this reaction for the semi-quantitative determination of lead dioxide in litharge. With slight modifications, this procedure may be applied to the determination of oxidizing agents generally when they occur in the presence of non-oxidizing substances.

Procedure. Boil about 5 g. of the litharge to be analyzed for 1 minute with a solution of 2 g. of aniline hydrochloride dissolved in 10 ml. of water and 5 ml. of concentrated hydrochloric acid. Cool, filter off any lead chloride, and compare the color of the filtrate with that of standards prepared by adding known quantities of lead peroxide to the aniline hydrochloride solution.

Detection of nitrites. Nitrites are detected by the yellow color which is formed when aniline is added to an acid solution containing a nitrite.[45-50] This reaction is based upon the formation of diazoaminobenzene. The test proposed by Deniges [47] is carried out as follows:

Reagent. Add 2 ml. of aniline to 40 ml. of glacial acetic acid and dilute to 100 ml. with water. Boil to destroy any color and store in a dark bottle.

Procedure. Boil 5 ml. of the reagent with 1 drop to 10 ml. of the solution to be tested. In the presence of nitrite, a straw-yellow to deep-orange color is formed. This is changed to red by the action of hydrochloric or sulfuric acid, but is restored by neutralizing with sodium carbonate.

The red is more delicate than the yellow color. By using 50 ml. of the reagent and 100 ml. of water that has been boiled 4 minutes and acidified with sulfuric acid, nitrite can be detected at a concentration of 1:5,000,000. Acid solutions should be neutralized with an alkali hydroxide or carbonate before addition of the reagent. Hypochlorite, hypobromite, chlorine and bromine disturb this reaction, although chlorate and nitrate do not interfere. The reaction is used to detect nitrite in the presence of iodide. When an aqueous solution of aniline sulfate containing 2-4 per cent sulfuric acid is added with an excess of ammonium hydroxide to a solution containing a nitrite, a yellow color and precipitate are formed.[45] Stone [46,82] uses the following modification of the Deniges [47] test:

Reagent. Mix 1 ml. of aniline, 1 g. of phenol, 15 ml. of concentrated hydrochloric acid and 150 ml. of water.

Procedure. Neutralize the solution to be tested, and add 0.5 ml. of the above reagent. If nitrite is present, a deep yellow color is produced when the mixture is made alkaline with sodium hydroxide solution.

Detection and determination of chromium and hydrogen peroxide. Chromates and dichromates react with an aqueous solution of aniline sulfate containing 2-4 per cent sulfuric acid to give a greenish-blue color. On the addition of ammonium hydroxide this changes to violet.[45] A similar reaction has been used by Leibov [51] for the colorimetric determination of chromic oxide. The reagent used is aniline hydrochloride.

Perchromic acid, which is formed by the action of hydrogen peroxide on chromates, when dissolved in an ether solution containing free acid rapidly converts aniline into a violet compound. This reaction has been used by Bach [52] for the detection of hydrogen peroxide in green plants.

Reagent. Dissolve 30 mg. of potassium dichromate and 5 drops of aniline in a liter of water.

Procedure. Mix 5 ml. of the reagent solution with 5 ml. of the solution to be tested. Then make acid with 1 drop of 5 per cent oxalic acid solution.

The color is also produced by chlorine, hypochlorites and the oxides of chlorine. Ilosvay [53,54] states that a pale violet color is obtained after three minutes in a hydrogen peroxide solution of 1 part per million, using the method of Bach.

Detection of persulfates. An orange-brown precipitate forms when a 2 per cent aqueous solution of aniline is added to a solution of a persulfate.[55,56] If the solution is very dilute, a brown color is obtained. The orange-brown precipitate may be extracted with benzene to give a compound which dissolves in hydrochloric acid to form a yellow color. This solution is permanently colored violet upon boiling.

Lenz and Richter [57] prepare a reagent for persulfates as follows: dilute 5 g. of 20 per cent sulfuric acid to 100 ml., add 10 g. of pure aniline and shake violently. Filter off the large drops of aniline which form to obtain a clear colorless acid solution. When added to an equal volume of a solution of ammonium persulfate and boiled, a distinct dark brown color is obtained. In this way 0.5 mg. of persulfate can be detected. Perborates and percarbonates give a very faint yellow color. Potassium perchlorate gives no reaction.

Detection of gold. Gold is detected by the permanent orange color which appears when an aqueous solution of aniline sulfate containing 2-4 per cent of sulfuric acid is added to a solution containing an auric salt.[45]

Detection of iron and vanadium. Vanadates react with aniline to form a blue to greenish-blue color which is used for the detection of vanadium.[58-63] The following procedure may be used: [58]

Procedure. Mix equal volumes of aniline and concentrated hydrochloric acid and place a drop of this solution on a strip of filter paper. Oxidize the solution to be tested by boiling with nitric acid, and place a drop of this solution over the drop of aniline hydrochloride. An intense blue color appears if vanadium is present. This test is capable of detecting 0.003 mg. of vanadium in 0.01 ml.

Cations do not interfere, but strongly oxidizing anions do. Nitric acid does not interfere.

The above reaction for vanadium has been used for the detection of vanadium in minerals.[59,60,63] The mineral is fused with sodium hydroxide, the mixture made acid with nitric acid and the test applied as directed above. If chromium or manganese is present it may be necessary to reduce any dichromate, manganate or permanganate by heating with concentrated hydrochloric acid, and then evaporating with nitric acid.[60]

Zilbermints and Florenzkii [59,63] have used the color produced by vanadic acid and aniline for the approximate determination of small quantities of vanadium in field work. Prepare the sample by boiling with 5 ml. of nitric acid, cooling, and repeating the treatment two more times.

Procedure. Impregnate a strip of filter paper with a few drops of saturated aniline hydrochloride solution in a mixture of 3 parts hydrochloric acid and 2 parts phosphoric acid. Place a drop of the solution to be tested in the center of the paper. A blue-green color forms if vanadium is present. A yellow-green color indicates the presence of iron, and a bright yellow ring shows the presence of a large quantity of copper. The approximate quantity of vanadium is found by comparing the color of the spot with that of a standard solution of ammonium vanadate in nitric acid.

Vanadium may be detected in steel by the aniline test without destroying the sample.[61]

Guyard[64] observed that the oxidation of aniline to aniline black is catalyzed by the presence of vanadium salts, and he used this effect for the indirect detection of vanadium.

More recently this reaction has been studied and applied to the analysis of vanadium by Szebelledy and Ajtai,[65,66] by Rosenthaler,[67] and Feigl: [68,69]

Procedure. To the solution to be tested add 2 ml. of 5 per cent aniline sulfate and 1 ml. of saturated potassium chlorate. Dilute to 5 ml. with distilled water. Prepare a blank using a similar quantity of the reagent, and distilled water instead of the unknown solution. On standing for 24 hours a brown color appears in the solution containing vanadium; the blank is yellow in color. The sensitivity of this reaction is 0.001γ.

Ferric iron accomplishes a similar acceleration and can be detected by a similar process. This reaction is sensitive to $3\text{-}4\gamma$ of ferric iron.[67] To eliminate interference by iron, add 0.05 g. of ammonium bifluoride. Ammonium chlorostannate also interferes, but this interference may be eliminated by the addition of 0.1 g. of potassium oxalate.

This test is modified by Rosenthaler[67] as follows:

Procedure. To 1 ml. of the solution to be tested, add 1 drop of aniline dissolved in 5 ml. of dilute nitric acid, and 1 ml. of 1 per cent potassium chlorate. Heat for 5 minutes on a water bath. Prepare a blank using distilled water instead of the unknown, and heat simultaneously on the water-bath. A lilac color appears in the solution containing vanadium.

The catalytic activity of vanadium in promoting the oxidation of aniline by potassium chlorate is increased by the addition of 8-hydroxyquinoline.[65] Under these conditions the reaction is said to be ten times as delicate.[65]

Detection of vanadium, tungsten and molybdenum. Aniline has been used with pyrocatechol acetate for the microchemical detection of molybdate, tungstate and vanadate: [70-72]

Procedure. Place a drop of a 01-1.0 per cent ammonium molybdate solution on a glass slide, and add a drop of a saturated solution of pyrocatechol acetate until an orange color appears. Then add pure aniline, avoiding an excess, and quickly remove the liquid from the crystals which form. Orange-colored, triclinic crystals indicate the presence of molybdenum. Tungstates and vanadium trichloride react similarly.

An aqueous solution of aniline sulfate containing 2-4 per cent sulfuric acid yields a greenish-blue color with vanadates. This changes to violet on the addition of ammonium hydroxide.[45]

Detection of hydrogen cyanide. Kozlovskii and Penner [73] have shown that aniline can be substituted for ammonia in the test for hydrogen cyanide. This test is based upon the catalytic effect of hydrogen cyanide in promoting the reaction between ammonia and alloxan to form characteristic crystals of oxaluramide.[73]

Detection of bromine and chlorine. Bromine may be detected by moistening a stirring rod with a solution of bromine water and placing the rod in a solution of aniline in water. An orange-yellow color forms if bromine is present.[74,75] Pozzi-Escot [76] has detected bromine by liberating the element from bromides by the action of chromic acid and sulfuric acid, and passing the bromine vapor over a few drops of a freshly prepared aqueous solution of aniline. The tribromoaniline which is formed may be observed microscopically as a mass of thin prisms.

Chlorine is detected by absorbing the gas in a solution of sodium hydroxide, moistening a stirring rod with this solution, and immersing the latter in a solution of aniline in water. A violet color forms with chlorine.[75] Ganassini [77] carries out the chlorine test as follows:

Procedure. Prepare a colorless solution of 2 ml. of aniline in hydrochloric acid and 4 ml. of water. Moisten filter paper with this reagent and expose to the gas suspected of containing chlorine. If chlorine is present, a wine-red color appears, and this quickly changes to blue in air.

Bromine yields a white compound, and nitrous oxide causes a yellow-brown and then a greenish-blue color.

A solution of 40 g. of phenol and 5 ml. of aniline in a liter of water gives a beautiful blue color with a trace of hypochlorous acid. This reaction is not affected by bromine.[78]

Detection of ammonia. Diazotized aniline yields a colored compound with ammonia which may be used for the detection of the latter.[79] The reagent is prepared by diazotizing aniline in the usual manner, and impregnating a strip of filter paper with this reagent. Upon exposure to air containing ammonia a colored product is obtained.

Detection of nickel. Nickel reacts with *o*-phenylenediamine and 1,3,4-toluylenediamine to form compounds which dissolve in aniline with a purple color.[80]

Aniline molybdate reacts with nickel salts to yield insoluble compounds similar to those precipitated by ammonium molybdate. These compounds are suitable for the detection of nickel.[88]

Determination of water. Kolthoff[81] has used aniline in a rapid method for the determination of water in glycerol. This is done by observing the temperature at which glycerol becomes immiscible with aniline. By preparing mixtures of glycerol and water of known content and observing the temperatures at which they become immiscible with aniline, a table may be prepared from which the water concentration can be read directly.

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o-ANISIDINE

Synonym: *o*-Methoxyaniline, *o*-Aminoanisole

C_7H_9ON Mol. Wt. 123.15 Beil. Ref. XIII, 358.

$$CH_3O—C_6H_4—NH_2$$

o-Anisidine is a yellowish liquid, which becomes brownish on exposure to air. It is volatile with steam and boils at 225° C. Its sp. gr. is 1.098. It is insoluble in water, but is miscible with alcohol and ether.

Detection of hydrogen cyanide. Hydrogen cyanide is detected by its catalytic effect in promoting the reaction between ammonia and alloxan to form characteristic crystals of oxaluramide. Various amines, including *o*-anisidine, have been substituted for ammonia in this test.[1]

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[1] M. T. Kozlovskii and A. J. Penner, *Mikrochemie.* 21, 82 (1936).

BENZIDINE

Synonym: *p,p'*-diaminodiphenyl

$C_{12}H_{12}N_2$ Mol. Wt. 184.23 Beil. Ref. XIII, 214(58).

$$H_2N—C_6H_4—C_6H_4—NH_2$$

Use: Detection of ammonia, cadmium, cerium, chlorate, chlorine, chromium, cobalt, copper, cyanate, cyanide, ferricyanide, ferrocyanide, fluoride, germanium, gold, iodate, iridium, lead, manganese, nickel, nitrate, nitrite, osmium, ozone, periodate, permanganate, persulfate, phosphate, platinum, silica, silver, sulfate, sulfite, thallium, thiocyanate, tungstate, vanadium and zinc.

Determination of barium, cadmium, chlorine, copper, cyanide, ferricyanide, ferrocyanide, fluoride, hydrogen chloride, nitrite, manganese, mercury, phosphate, potassium, selenate, silica, sodium, sulfate, thiocyanate and tungstate.

Benzidine is a white or slightly reddish crystalline powder which darkens on exposure to air and light. It melts at 115-120° C. when slowly heated, but melts at 128° C. when anhydrous and rapidly heated. It is only very slightly soluble in cold water, but more soluble in boiling water, alcohol, and ether. Benzidine hydrochloride is commonly used as an analytical reagent because of its solubility in water.

Preparation. *Hydrazobenzene:* Dissolve 50 g. of sodium hydroxide in 150 ml. of water. Pour the warm solution into a flask, and add 50 ml. of alcohol and 41 g. of nitrobenzene. The flask should have a capacity of 1 liter and should be fitted with a stirrer and a Leibig condenser, which is clamped obliquely for reflux. An opening which can be closed with a cork should also be provided for the addition of zinc dust. Now add 6-8 g. of zinc dust with stirring, and keep the reaction mixture at the boiling point by the continuous addition of zinc dust. The reaction should not be allowed to become too violent, and should not be completely interrupted by cooling the reaction mixture. About 100-120 g. of 75 per cent zinc dust is required for the complete reduction of the nitrobenzene. If the reaction should cease prematurely, heat the flask on a vigorously boiling water-bath. It is essential for a good yield that the mixture be stirred continuously during the reduction.

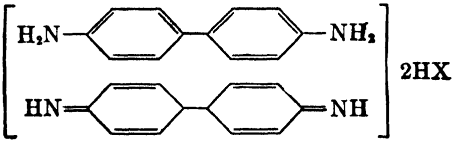
When reduction is complete, as indicated by the pale yellow color of the solution, heat the mixture on a water-bath and add 500 ml. of alcohol. Filter while boiling hot through a Buchner funnel, and wash the flask with 50 ml. of hot alcohol, which is then poured over the excess zinc dust on the funnel. Allow the filtrate to cool in a closed flask which is placed in a freezing mixture. Allow to stand for 1 hour and filter the hydrazobenzene with suction. Wash the crystalline powder several times with 50 per cent alcohol to which a little aqueous sulfurous acid has been added until the filtrate is no longer alkaline. Dry *in vacuo*.[1]

Benzidine: Dissolve 9.2 g. of hydrazobenzene in the smallest possible quantity of ether, and add dropwise with shaking to 100 ml. of ice-cold 1:1 hydrochloric acid. Add 50 ml. of concentrated hydrochloric acid and allow the mixture to stand for 30 minutes. The benzidine hydrochloride which precipitates is then filtered with suction and washed, first with 1:1 hydrochloric acid, and then with a little ether. Purify the product by dissolving in hot water and recrystallizing by adding hydrochloric acid to the slightly cooled solution.

The free base is obtained as follows: add a slight excess of concentrated sodium hydroxide solution to a not too concentrated solution of benzidine hydrochloride in warm water containing a little hydrochloric acid, and then cool rapidly to 15-20° C. Filter the precipitate with suction and wash free of alkali with water.[2]

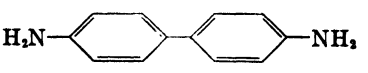
Analytical reactions of benzidine. The analytical applications of benzidine depend upon three characteristics of the benzidine molecule: (a) its susceptibility to oxidation; (b) its ability to form complexes with metallic salts; and (c) its salt-forming qualities.

Benzidine is converted by a number of oxidizing agents, as well as by an auto-oxidation process, into a blue oxidation product formed from one molecule of the amine, one molecule of the imine acid, and two equivalents of acid, according to the following formula[3]



where X is a univalent acid radical. Such oxidizing agents as lead peroxide, manganese dioxide, chromates, vanadates, periodates, iodates, persulfates, chlorates, and permanganates may be detected by means of the blue color which they yield with benzidine. Bivalent manganese, cerium, and cobalt, and trivalent cerium, and thallium may be detected with the aid of this reagent in the presence of a base by means of an auto-oxidation process which converts the benzidine into the blue oxidation product.[4]

Benzidine is capable of taking the forms



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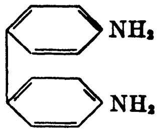

II

The equilibrium position corresponds to formula II, which explains the fact that the two amine groups react instantaneously with metallic salts to form complex amines. The following compounds have been prepared by Spacu[6] and Barcelo,[7] in which Bzd represents the benzidine molecule:

$[ZnBzd]Cl_2$
$[ZnBzd]_2Br_2$
$[ZnBzd]SO_4$
$[CoBzd](SCN)_2$
$[CoBzd(H_2O)_2](SCN)_2$
$[CoBzd(H_2O)_2](SCN)_2 \cdot 2H_2O$
$[CoBzd_3]Br_2 \cdot 4H_2O$
$[CoBzd](NO_3)_2$
$[FeBzd](NO_3)_3$
$[FeBzd(H_2O)_2](NO_3)_3$
$[HgBzd](CN)_2$
$[AgBzd](NO_3)$
$[CuBzd]SO_4$
$[CuBzd(H_2O)_2](CH_3CO_2)_2$
$[MnBzd(H_2O)_2]Cl_2$
$[MnBzd_2]Br_2$
$[MnBzd_3](NO_3)_2 \cdot 4H_2O$
$[CdBzd]Cl_2$
$[CdBzd]SO_4$
$[MgBzd_3]Br_2 \cdot 6H_2O$
$[MgBzd_3]I_3 \cdot 6H_2O$
$[MgBzd_3](ClO_3)_2 \cdot 4H_2O$

Benzidine also forms insoluble salts with a number of anions, such as sulfate, tungstate, phosphate, selenate, ferrocyanide, and ferricyanide, and may be used for the quantitative precipitation of these ions.

Hovorka[248] prepared and studied the reactions of a number of derivatives of benzidine. Especially, the reactions with selenate, sulfate, tungstate, molybdate, vanadate, chloride, bromide and iodide were investigated.

Detection of manganese. The manganous ion in the presence of a base is capable of oxidizing benzidine to the blue meriquinoid oxidation product by means of an auto-oxidation process. The precipitated manganous hydroxide is converted by contact with air into hydrated manganese dioxide, according to the following equation,

$$Mn(OH)_2 + (O) \rightarrow MnO(OH)_2$$

and $MnO(OH)_2$ reacts with the benzidine to form the blue oxidation product. This reaction has been used by several investigators as a test for manganese.[8-17,227,230,231,241] It is not in any sense specific for manganese, however, since it is given by those elements which yield compounds which are auto-oxidizable and also with certain oxidizing agents.[18]

Manganese may be detected by the following procedure:

Reagent. Dissolve 0.05 g. of benzidine base or hydrochloride in 10 ml. of acetic acid and dilute to 100 ml. with water. Filter before use.

Procedure. Add a dilute solution of sodium hydroxide to 50-100 ml. of the solution to be tested until the mixture is alkaline, and then heat to boiling. Filter, and add a drop of the benzidine reagent to the precipitate which is retained on the filter paper. An intense blue color appears if manganese is present, but this disappears soon if the cation is present in low concentration. The test is made somewhat more satisfactory by using a sodium hydroxide solution containing a trace of silicate or carbonate in order that the precipitated silica or calcium carbonate may adsorb the colored compound. By means of this reaction 1 part of manganese in 125,000,000 parts of water can be detected.

Cerium, cobalt and thallium interfere by giving similar color reactions.

A spot test for manganese is generally more satisfactory than one carried out on a macro-scale in a test tube, since in the latter case the color is usually only transitory whereas the color in the spot test is more stable.[9]

Reagent. Dissolve 0.05 g. of benzidine or benzidine hydrochloride in 10 ml. of acetic acid, dilute with water to 100 ml. and filter.

Procedure. Mix a drop of the solution to be tested on a strip of filter paper with a drop of 0.05 N sodium hydroxide solution and warm. Then add a drop of the benzidine solution and again warm. A blue color appears if manganese is present, and the intensity of the color depends upon the amount of manganese present. The color fades on drying, but reappears on the addition of more of the benzidine reagent. By means of this reaction 0.15γ of manganese can be detected at a concentration limit of 1:330,000.

The reaction between manganese and benzidine cannot be used in the presence of other oxidizing agents or auto-oxidizable substances which also oxidize benzidine. These include chromates, ferricyanides and cobalt, thallium, silver and cerium salts. If these ions are present along with the manganese, a special procedure must be employed whereby the interference is eliminated.

In addition to the above-mentioned substances, certain other cations which yield indifferent metallic hydroxides may also interfere by masking the manganese hydroxide, and thereby reducing the sensitivity of the test. Typical of this group is ferric hydroxide, which, although it has no effect upon benzidine, reduces the sensitivity of the manganese test to such an extent that only 2.5γ of manganese can be detected when 250γ of iron are present. In the absence of ferric iron 0.15γ of manganese can be detected. If the precipitation of iron hydroxide is prevented by the addition of Rochelle salt, which can be effected directly upon the filter paper, as little as 1γ of manganese can be detected in the presence of 1000 times as much iron. Ferric chloride, however, and other soluble ferric salts may oxidize benzidine with the formation of colored products.

Dobbins and Southern[20] have used benzidine as a confirmatory test for manganese in a systematic scheme of qualitative analysis.

Glazunow[21,22] has proposed an electrometric method for determining manganese in metals and alloys. This method consists in clamping the metal together with a strip of filter paper impregnated with benzidine between the poles of a battery, and after a time treating the paper with sodium peroxide. Wenger and coworkers,[23] have made a critical study of all of the various methods used for detecting manganese and recommend the use of benzidine both as a spot test and for a test tube procedure. The procedure of Glazunow, however, is not recommended. Zinc, iron and other elements of the same group give the same reaction; and, while the reaction is positive, it is of less interest than other tests which have been used.

Feigl [19] has used the benzidine reaction as the basis for the microdetection of manganese.

Procedure. Place a drop of the manganese solution on a microscope slide and add a drop of dilute potassium hydroxide solution. Allow the solution to evaporate a little, and add a drop of benzidine acetate solution. A blue coloration appears with only a trace of manganese.

Detection of manganese in the presence of cobalt. Under the normal conditions of the manganese test, cobalt hydroxide is auto-oxidizable and yields a test similar to that obtained with manganese. In order to detect manganese in the presence of cobalt, the latter should be converted into stable $K_3[Co(CN)_6]$ by adding potassium cyanide and warming the mixture. An excess of potassium cyanide interferes with the manganese test by forming a complex manganese compound, and so it must be removed by the addition of a few drops of concentrated hydrochloric acid (hood). This destroys the cyanide, and any manganese cyanide which has been formed, while the complex cobalt ion remains unaffected. The steps in this procedure are conveniently carried out in a microcentrifuge tube. On standing for a time, the potassium cyanide solution of the complex cobalt salts gradually develops a reddish-violet color with benzidine. By means of the above procedure 0.5γ of manganese can be detected in the presence of 1200 times as much cobalt.

Detection of manganese in the presence of cerium. In order to detect manganese in the presence of cerium, which forms the auto-oxidizable $Ce(OH)_3$, the solution to be tested must first be warmed for 2-3 minutes with a little calcium fluoride, which brings about the precipitation of the cerium as insoluble cerium fluoride. When the solution is filtered, the cerium fluoride, and any unchanged calcium fluoride, are retained on the paper and the manganese test is carried out on the filtrate according to the usual procedure. By this method 5γ of manganese can be detected in the presence of 1000 times as much cerium.

Detection of manganese in the presence of copper. Copper may interfere with the manganese test, due to the formation of copper hydroxide and insoluble basic copper acetate, which may mask the color of the blue benzidine oxidation product. To detect small quantities of manganese in the presence of large amounts of copper, the test is performed as described above when cobalt is present. Interference by the cupric salt is prevented by the formation of $K_3[Cu(CN)_4]$ and $Cu_2(CN)_2$. In this way 1.6γ of manganese can be detected in the presence of 800γ of copper.

Detection of manganese in the presence of silver and thallium. Both silver and thallium interfere with the manganese test, since the oxidizing substances Ag_2O and $Tl(OH)_3$ and the auto-oxidizable TlOH may react with the benzidine to yield a blue color. This interference is eliminated by first precipitating silver and thallium as the chlorides, filtering, and applying the benzidine test to the clear filtrate. Thallic salts are first reduced to thallous sulfate with sulfur dioxide, and are then precipitated with sodium chloride. The sensitivity of the manganese test is not appreciably changed by this treatment. The manganese test should be applied to the clear filtrate after the precipitation of silver and thallium, rather than by precipitating silver and thallium chlorides directly on filter paper, since both of the insoluble chlorides react slowly with benzidine to yield a blue color. This seems to be due to the photochemical dissociation of thallium and silver chlorides to yield a small quantity of free chlorine, which is sufficient to oxidize benzidine.

Detection of permanganates. Permanganates are detected, after reduction to manganous salts, by means of the benzidine reaction. The following method may be used for the detection of permanganates in the presence of chromates:[216]

Procedure. Acidify the solution to be tested and apply a drop to a strip of filter paper. Hold the moist portion of the paper over a beaker containing sulfurous acid for a few minutes to reduce the chromium and manganese, and then dry in an oven to expel the excess sulfur dioxide. Proceed with the detection of manganese by the method described above. By this method 0.5γ of manganese can be detected in the presence of 250 times as much chromate.

Determination of manganese. When benzidine hydrochloride is added to a very dilute solution containing the permanganate ion, a brilliant blue-green color results. This reaction may be used as the basis for a colorimetric determination of manganese.[24] The reaction is sensitive to 8 parts of manganese in 1 billion parts of solution. The blue-green color produced by benzidine is much more brilliant, and consequently more favorable for the colorimetric estimation of manganese, than the natural color of the permanganate ion, or its combination with *o*-tolidine in very dilute solutions. The one great disadvantage of this procedure is the instability of the coloration produced. In about 2 minutes the blue-green color changes to a yellowish-green, and this also is unstable. Since the color fades so rapidly, it is necessary to employ artificial standards from copper sulfate and picric acid.

Reagents. *Benzidine reagent:* Dissolve 2.3 g. of benzidine base in 100 ml. of 5 per cent hydrochloric acid.

Artificial standard: Add to a 15 per cent cupric sulfate solution the proper amount of 0.5 per cent picric acid to produce the correct tint. When the identical blue-green tint is obtained, dilute the standard to such concentration that 100 ml. will match in depth the amount of color produced by 0.001 mg. of permanganate in a solution of known permanganate content. Each ml. of standard used in matching the color produced by benzidine is equal to 0.0001 mg. of permanganate ion. This standard keeps indefinitely.

Procedure. Use a suitable aliquot of the material to be analyzed so that the amount of permanganate taken lies between 0.0001-0.001 mg. Dilute to 100 ml. and add 1 drop of the reagent. Immediately transfer the mixture to a comparison tube and match against the standard.

This procedure cannot be carried out on solutions containing sulfates, since benzidine reacts with the sulfate to produce an insoluble salt. The above method is more delicate than that employing potassium iodate, which is based upon the oxidation of manganese to permanganate,[25] but it is generally less satisfactory due to the rapid fading of the blue color.[26] Despite the fact that the brilliance of the color produced with benzidine is more favorable than that of the permanganate ion, the latter method generally is to be preferred.

Detection of cerium. Both ceric hydroxide and the auto-oxidizable cerous hydroxide are capable of converting benzidine into the blue meriquinoid compound which has been described in the test for manganese. Consequently benzidine may be used as a reagent for the detection of cerium.[8,13,27,28] In addition to the hydroxides of cerium, other ceric and cerous compounds give color reactions with benzidine with the exception of ceric fluoride, ceric sulfate and ceric bisulfate. The most sensitive reaction is obtained by making the solution of the cerium salt alkaline, boiling the mixture, filtering a portion, and then adding a few drops of a solution of benzidine in acetic acid to the filter paper upon which the hydroxides of cerium are retained. By means of this procedure as little as 0.02 mg. of cerium in 1 liter of solution can be detected.

Cerium may also be detected by means of a spot test.

Reagent. Dissolve 0.05 g. of benzidine or benzidine hydrochloride in 10 ml. of acetic acid, dilute to 100 ml. with water, and filter.

Procedure. Place a drop of the solution to be tested on a strip of filter paper, add 1 drop of a 0.05 N potassium or sodium hydroxide solution, and then add 1 drop of the benzidine solution. According to the cerium content, a more or less deep blue coloration results. By means of this procedure, as little as 0.18γ of cerium can be detected at a concentration of 1:275,000.

Manganese, cobalt, copper, silver and thallium salts and chromates are capable of converting benzidine into the blue oxidation product, and consequently interfere with the benzidine test for cerium. Weakly acid solutions of iron salts also give a similar color reaction, although alkaline solutions do not. In the presence of these interfering substances, cerium is precipitated as cerous fluoride with hydrofluoric acid from the neutral or slightly acid solution to be tested and the residue is then treated with sodium hydroxide and the resulting mixture tested with benzidine.

Cerium may be detected in the presence of ferric iron by means of the following procedure:

Procedure. Add sodium hydroxide to a solution containing trivalent cerium and iron until a permanent precipitate is formed, then add a few drops of hydrofluoric acid and boil the mixture. Filter and wash the precipitate once with water. Cover with dilute alkali, and add a few drops of a solution of benzidine in acetic acid. In this way 70γ of cerium can be identified in the presence of 227 mg. of iron.

The metals of the rare earths, including lanthanum, thorium, zirconium, yttrium, neodymium and praseodymium do not give a color reaction with benzidine, and consequently cerium can be detected in the presence of metals of the rare earths by means of this reagent.

Detection of cobalt. Cobalt salts, like the salts of manganese, copper, cerium, thallium, and chromium are capable of converting benzidine into a blue oxidation product. This reaction is used for the detection of small quantities of cobalt.[8]

Reagent. Dissolve 50 mg. of benzidine in 10 ml. of acetic acid, and dilute with water to 100 ml.

Procedure. Add a dilute solution of sodium hydroxide to 50-100 ml. of the solution to be tested until the mixture is alkaline, and then heat to boiling. Filter, and to the residue add a drop of the benzidine solution. An intense blue color forms if cobalt is present. By means of this procedure 1 part of cobalt in 30,000,000 parts of water can be detected.

Manganese, cerium, thallium, chromium and other oxidizing agents give a similar reaction and must be absent while applying the test. The following test has been proposed by Tananaev [29] for detecting cobalt in nickel salts which are free from chromium, manganese, lead and silver.

Procedure. Add a little dry sodium peroxide to 1-2 ml. of a neutral or alkaline solution to be tested and acidify with acetic acid, and then add a little benzidine. A blue color forms if cobalt is present. By means of this method 0.01 mg. of cobalt in pure solutions, and 0.2 per cent of cobalt in nickel salts can be detected.

A solution of a cobalt salt when treated with a dilute alcoholic solution of benzidine or with an alcoholic solution of dimethylglyoxime does not become colored, but if these two reagents are added together a beautiful orange-red coloration appears. Chiarottino [30,31] has used this reaction to identify as little as 0.1 mg. of cobalt. The details of this test are given in the section on dimethylglyoxime.

Detection of nickel. If solid nickelic hydroxide, $Ni(OH)_3$, is treated with an acetic acid solution of benzidine, an intense blue color develops. This reaction may be used for the detection of nickel, but appears to offer no advantages over many other superior methods.[32]

Glazunow [21,22] and Arnold [33] have used benzidine as a reagent for detecting nickel in metals and alloys by means of an electrographic imprint method. A strip of filter paper which has been saturated with a 10 per cent solution of benzidine in acetic acid is clamped with the metal to be tested between the poles of a battery. The presence of nickel is indicated by the gray-blue or blue color formed by the passage of the nickel ions into the paper due to the action of the electric current. A black color appears if the paper is treated with sodium sulfide or a red color if the paper is treated with ammoniacal dimethylglyoxime. By means of this method 0.1γ of nickel can be detected without the destruction of the sample. Wenger and coworkers,[34] have studied many methods which have been proposed for the detection of nickel and recommend this procedure.

Detection of copper. The blue oxidation product of benzidine is formed when the latter compound is present during the conversion of cupric to cuprous compounds by means of the alkali iodides, bromides, chlorides, cyanides, thiocyanates, cyanates and selenocyanates. The sensitivity of the reaction decreases with the halogens from the iodide, which is most sensitive, to the chloride which is least sensitive. A violet precipitate is obtained with cyanates. With cyanides a blue precipitate is formed, and this rapidly disappears when the cupric ion is reduced to the cuprous state and is finally combined as $Cu(CN)_4^{-3}$.

The oxidation potential of cupric ions is not sufficient to bring about the conversion of benzidine to benzidine blue, but it is greatly increased by the formation of insoluble cuprous halides.[35] The reactions comprising the test appear to take place in two steps: (a) benzidine reacts with copper to form a compound in which the copper is a part of the cation; and (b) copper and halogen are split off due to the formation of the cuprous salt, and there is a corresponding oxidation of benzidine to its blue oxidation product.[36] Copper is detected in a spot test by means of the following procedure: [37,230]

Reagent. Dilute 10 ml. of a 10 per cent solution of benzidine in ethyl acetate with 100 ml. of water and shake well. Filter the solution from the undissolved benzidine and ester.

Procedure. Place a drop of the solution to be tested on a strip of filter paper, add a drop of the reagent solution, and a drop of saturated solution of potassium bromide. A blue spot or ring is formed if copper is present. A blank test should be carried out if the concentration of the copper is very low. By means of this test as little as 0.6γ of copper can be detected at a concentration of 1:75,000.

Silver, mercurous, iron, thallium, ceric and silver salts and chloroplatinic acid interfere with this reaction. Silver ions may be removed by precipitation as the insoluble chloride; and interference due to iron salts may be eliminated by the addition of an alkali fluoride. Other strongly oxidizing cations, which interfere due to oxidation of benzidine, may be rendered harmless by reducing with bismuth amalgam. Manganese salts interfere only when present in considerable quantity, and then they give a blue color with benzidine only after standing for some time.

Fleming[38] has used ammonium or potassium thiocyanate instead of the halide for this reaction. A deep blue precipitate, which is insoluble in the usual organic solvents, is formed on the addition of 3-4 drops of dilute ammonium thiocyanate solution and a few drops of 1 per cent alcoholic benzidine to a little of a dilute aqueous solution of a cupric salt. This test is obtained with 1 part of copper in 1,000,000 parts of solution.

Spacu[39] has found that if a dilute solution of a copper salt is treated with potassium iodide and then a little freshly prepared 1 per cent alcoholic benzidine solution, a flocculent dark blue precipitate is formed. Spacu has assigned to this compound the formula $[CuBzd]I_2$, in which Bzd = benzidine. According to Tettamanzi[40] the reaction of copper with benzidine and potassium iodide is not due to the formation of the copper complex, but rather to the formation of the blue quinhydrone as described by Willstatter and Piccard.[41] He claims that the reaction is not characteristic for copper at all, but that a similar blue compound is formed with iodine and benzidine alone. Spacu[42] on the other hand, claims that in the presence of cupric ions, a blue precipitate is obtained even at a dilution of 1:2,000,000, while with benzidine and iodine at a dilution of 1:1,000,000 only a blue color develops and that this immediately disappears. In the opinion of Spacu this is evidence that the complex copper benzidine iodide is actually formed.

Rosenthaler[43] has used benzidine and a cyanide in a microtest for copper. The sensitivity of this reaction is 1:40,000.

Determination of copper. When solutions of copper salts are treated with benzidine and thiocyanate or iodides, copper is quantitatively precipitated as the deep blue flocculent compounds, $[CuBzd](SCN)_2$, and $[CuBzd]I_2$. These precipitates may be filtered off, ignited to copper oxide and weighed.[44,45,235,237]

Procedure. To 50-75 ml. of an aqueous solution of a copper salt, containing not more than 10 mg. of copper, add 40-50 ml. of a 1 per cent ammonium thiocyanate solution, and then add 10-20 ml. of a 2 per cent alcoholic solution of benzidine. The amount of thiocyanate added should correspond to approximately 4-5 times the theoretical value, but benzidine should be used only in slight excess. Filter off the blue precipitate which forms, wash thoroughly with water, dry, ignite to constant weight, and weigh as CuO.

The results obtained by this method are said to be excellent. The microdetermination is carried out in an exactly analogous manner.[245]

Shakhkeldian[46] has proposed the following colorimetric method for determining very small quantities of copper. Prepare a test solution and a standard solution simultaneously as follows:

Procedure. The standard solution should contain 0.003 mg. of copper per ml. in the form of $CuSO_4 \cdot 5H_2O$, and the copper in the unknown solution must be in the form of copper sulfate. Add to 50 ml. of both standard and the unknown solution 10 ml. of 3 per cent sodium salicylate solution, 10 ml. of ammonium hydroxide ($d = 0.9$), 3 ml. of 0.1 per cent colorless benzidine solution in 20 per cent acetic acid, and 1-1.5 ml. of 1 per cent potassium cyanide solution. Dilute each mixture to 100 ml. and compare in a colorimeter. The addition of the reagents and the colorimetric determination must be completed within 5 minutes, since the colors formed in this reaction are very unstable. A standard can be prepared from an acidified solution of methyl orange.

The alkali and the alkaline earth metals do not interfere with this procedure but silver must be removed. The heavy metals are removed by making the solution distinctly alkaline with ammonium hydroxide and boiling for 5 minutes.

The colorimetric method may be used with solutions containing 0.0002-0.02 mg. of copper per ml. where other methods are unreliable. The results obtained are 25-33 per cent higher than those obtained using the method of Bertrand and Mokragnatz,[47] which is based upon the precipitation of copper with pure calcium hydroxide.

Maier [48] has found the method of Shakhkeldian useful for the determination of copper in rain water which has been collected on trees that have been sprayed with copper compounds. Maier has found that the color which is developed in this method changes quickly in intensity, and varies with the age of the sodium salicylate solution and the quantity of potassium cyanide that is present. The method may, however, be used satisfactorily with careful attention to detail.

Detection of lead. Lead peroxide is one of the several oxidizing agents which are capable of converting benzidine into the blue meriquinoid oxidation product. Consequently, lead may be detected by means of benzidine after first converting to lead peroxide by means of an alkali hypobromite.[3,35,229,230,242,246] An alkali and bromine water are recommended for the conversion of the lead compound to lead peroxide, since the excess bromine is easily removed with ammonia according to the following reaction:

$$3NaBrO + 2NH_3 \rightarrow 3NaBr + N_2 + 3H_2O$$

Procedure. Place a drop of the solution to be tested on a strip of filter paper, and add a drop of 3 N sodium hydroxide solution and a drop of a saturated solution of bromine in water. Allow to stand for a moment and add 2 drops of 1:1 ammonium hydroxide solution. Warm the paper carefully over a small flame until the excess ammonia has been removed, and then add a drop of a solution of benzidine in acetic acid. A blue spot appears if lead is present. The blue color fades if the amount of lead is very small. By means of this reaction 1γ of lead can be detected at a concentration of 1:50,000.

Cerium, manganese, bismuth, and thallium salts interfere with this test, since under the same conditions these metals are converted to their higher oxides, which are also capable of oxidizing benzidine. Interference due to cerium, manganese and bismuth, however, may be eliminated by treating the solution of the salts with an excess of sodium hydroxide solution. Cerium, manganese and bismuth salts are precipitated as the hydroxides, while lead remains in solution as the plumbite. The test can therefore be carried out on the alkaline filtrate obtained from this mixture without interference from the above metals.

The test is made more sensitive by the following procedure:

Procedure. Treat the solution to be tested with 3 ml. of 3 N sodium hydroxide solution and 2 ml. of saturated bromine water and boil a few minutes. Filter through a quantitative filter paper, wash the residue with hot 1:1 ammonium hydroxide solution, and then with water. Add a drop of an acetic acid solution of benzidine to the residue on the paper. If only 10γ of lead is present in 10 ml. of solution, an appreciable blue coloration appears. The sensitivity of this test is 1:1,000,000.

Leitmeier and Feigl[49] have used a method based upon the reaction of lead peroxide with benzidine for the detection of small quantities of lead in minerals and rocks.

Procedure. The finely powdered material is heated slightly with 2 drops of saturated bromine water and 1 drop of sodium hydroxide, and then warmed with 1 drop of ammonium hydroxide solution. A blue color appears on the addition of a drop of a solution of benzidine in acetic acid if lead is present.

Manganese reacts with the reagent without treatment with bromine and must be absent when making the test.

Detection of thallium. Thallic compounds may be detected after conversion to thallic hydroxide by a reaction based on the oxidation of benzidine to benzidine blue. Thallous salts may also be detected by this reaction, but they must first be oxidized with the aid of aqua regia.[5,8,238] The benzidine reaction for thallium is recommended by Wenger and co-workers.[256]

Procedure. Place a drop of ammonium hydroxide on a strip of filter paper and add a drop of the solution to be tested. Then add a drop of a filtered solution of benzidine in dilute acetic acid. A blue ring or spot is formed if thallium is present. By means of this reaction 0.3γ of thallium can be detected at a concentration of 1:166,000.

Manganese, cobalt, cerium, and silver salts must be absent, and other oxidizing agents which are capable of converting benzidine into the blue compound must also be absent.

Detection of chromium. A solution of benzidine in acetic acid is oxidized to the blue quinoid compound by means of chromates. Since all chromic salts are easily converted to chromates by means of sodium peroxide, the benzidine-chromate reaction constitutes a sensitive and a simple test for chromium.[14,50,51,113,244]

Reagent. Dissolve 0.05 g. of benzidine or benzidine hydrochloride in 10 ml. of acetic acid and dilute to 100 ml. with water. Filter before use.

Procedure. Place a drop of a moderately concentrated, freshly prepared solution of sodium peroxide, and a drop of the solution to be tested on a strip of filter paper. The chromate ion, which is formed in this reaction, diffuses into the outer zone of the moist area and is identified by the blue ring which forms upon the addition of a drop of the acetic acid solution of benzidine. By means of this reaction 0.25γ of chromium can be detected at a concentration of 1:200,000.

Vanadates, like chromates, also oxidize benzidine to benzidine blue, and must therefore be absent in making the chromium test. Lead, cobalt, silver, and copper salts, which also give a blue color with benzidine under the conditions of the test, do not interfere due to the capillary separation of chromate in the paper. Manganese, however, interferes, since the manganese dioxide which is formed diffuses into the outer zone; and, although invisible, it reacts with benzidine in the same manner as chromate. A special method therefore is required for detecting chromium in the presence of manganese.

Procedure. Place a drop of the solution, which may contain cations of all groups, on a watch glass and add an excess of sodium peroxide. Stir with a glass rod with gentle heat, and then remove a drop from the mixture and place upon a strip of filter paper. The dark precipitate which remains in the drop forms a dark spot on the filter paper, while the clear liquid, which contains the chromium, forms a colorless zone about the dark area. Place a drop of an acetic acid solution of benzidine outside of the moist area in such a manner that the two solutions mix by diffusion. When the reagent diffuses into the original spot, a blue ring is formed and this slowly extends to the center of the spot.

According to Kuhlberg [52] the sensitivity of the chromate-benzidine reaction is markedly increased by adding a mixture of benzidine and hydrogen peroxide instead of pure benzidine. This appears to be due to the formation of the unstable perchromates, which have a greater oxidation potential than the chromate. The test is carried out by substituting a mixture of equal parts of 1 per cent alcoholic benzidine and 30 per cent hydrogen peroxide for the benzidine-acetic acid solution used in the test described above. According to Kuhlberg, the test is about 70 times as delicate as the *o*-tolidine reaction.

The reaction between chromates and benzidine may be used for the detection of chromium in steel.[53,54]

Procedure. Place 2-3 drops of 33 per cent sulfuric acid on the clean surface of the steel to be tested; and, after 2 or 3 minutes, add 2-3 drops of a concentrated solution of sodium peroxide (excess). Mix thoroughly and transfer the mixture to a strip of filter paper. Place a drop of a saturated solution of benzidine in 50 per cent acetic acid near the edge of the moist area. A blue color at the zone of contact of the two liquids indicates chromium. The sensitivity of this test is 0.1γ of chromium.

Van Eck [55] has used benzidine as a reagent for the microdetection of small quantities of chromates. The blue crystalline deposit which is formed in the reaction between chromates and benzidine is identified microscopically.

The color reaction between benzidine and chromate has been studied as the basis of a possible procedure for the colorimetric determination of chromium, but Leibov [286] claims the method is not sufficiently sensitive to be of much value.

Detection and determination of gold. Auric salts oxidize acetic acid solutions of benzidine to the blue oxidation product. This reaction is used for the detection of gold.[56-60]

Procedure. Place a drop of the solution to be tested on a strip of filter paper, and add a drop of a 0.05 per cent solution of benzidine in 10 per cent acetic acid. A blue color is formed with as little as 0.02γ of gold in 0.001 ml. The concentration limit is 1:50,000.

The interference with this test is essentially the same as that discussed in the preceding sections. Many oxidizing agents and auto-oxidizable substances give the same reaction.

A number of methods have been proposed for the approximate determination of small quantities of gold by means of spot tests.[60,61,62] The coloration produced by a drop of solution upon a strip of filter paper that has been impregnated with benzidine is matched with the color of spots produced by a series of standard gold solutions. This method is accurate to within approximately ±2 per cent for quantities of gold ranging as high as 0.1 mg., but the error increases to ±20 per cent when the gold content is 0.06 mg. Efforts to determine gold gravimetrically by weighing the blue precipitate which is formed in the reaction between gold salts and benzidine have proved unsuccessful.[45]

Plank [63] has proposed a colorimetric method for the determination of small quantities of gold based upon the reaction between gold and benzidine.

Procedure. Evaporate a solution of gold chloride to remove excess acids, transfer to a volumetric flask, and fill to a little over half its volume with distilled water. Then add a dilute hydrochloric acid solution of benzidine, shake well, and allow the mixture to stand for two hours. Dilute to the mark and measure the resulting color in a Pulfrich photometer, using color filter S50. The color of this solution does not obey Beer's law, and so special curves must be prepared by measuring solutions of known gold content which are similarly treated.

The color reaction based upon the oxidation of benzidine is disturbed by the presence of heavy metals, and certain electrolytes, such as the salts of alkali metals. Consequently in the colorimetric determination of gold it is essential that these substances be absent.[64]

Glazunow [21,22] and Arnold [33] have used an electrographic imprint method for the determination of gold in metals and alloys. When a strip of filter paper that has been impregnated with a 1 per cent solution of benzidine in 10 per cent sodium chloride solution is clamped with strips of the metal to be analyzed between the poles of a battery, a dark blue stain appears if gold is present in the metal. Many other metals interfere with this test.

Detection of osmium. A violet color is obtained when osmium reacts with a solution of benzidine in acetic acid. This reaction has been used by Tananaev and Romaniuk [65] as a sensitive test for osmium. Ruthenium, gold and silver give a similar test, and consequently interfere with the ordinary drop reaction, but if the test for osmium is made with vapor from a solution containing the osmium salt this interference can be eliminated.

Procedure. Place 1-2 ml. of the solution to be tested in a small test tube which is fitted with a stopper carrying a short length of glass tubing which terminates with a very narrow opening on the outside. Moisten a strip of filter paper with a little benzidine in dilute acetic acid and bring the end of the tubing against the moistened part of the filter paper. Heat the solution in the tube and allow the vapor to impinge upon the spot. A blue coloration appears within 30 seconds if osmium is present. By means of this reaction as little as 0.08γ of osmium in 0.001 ml. can be detected.

Detection and determination of iridium. Tetravalent iridium may be detected in concentrations as low as 0.001 per cent in aqueous solutions by means of the formation of a sky-blue color with benzidine. Bivalent platinum does not give a similar color, although with high concentrations of platinic salts a rose precipitate is obtained. Tetravalent iridium and rhodium give a green color and rose-yellow precipitate respectively. Osmium tetroxide produces a blue color similar to that obtained with iridium.[66]

Khlopin [66] has used the reaction between benzidine and iridium for the determination of iridium in platinum.

Reagents. *Benzidine reagent:* Dissolve 1 g. of benzidine in 10 ml. of glacial acetic acid and 50 ml. of water. This solution should be used within 24 hours.

Standard platinum solution: Dissolve 1.0 g. of pure ammonium chloroplatinate (iridium-free) in distilled water and dilute to 1 liter.

Procedure. To determine the iridium content of metallic platinum, dissolve 0.04397 g. of the metal in aqua regia, and evaporate just to dryness. Add hydrochloric acid and again evaporate just to dryness. Dissolve the residue in distilled water, neutralize with ammonium hydroxide, and dilute to 100 ml.

To analyze a solution of a platinum salt which contains some iridium, concentrate or dilute until the platinum concentration corresponds to 0.1 per cent ammonium chloroplatinate. If the state of oxidation of the iridium is not known, heat the solution to 70-80° C. and pass chlorine gas through the mixture until oxidation is complete. Remove excess chlorine with a stream of air or carbon dioxide. It is important that all chlorine be removed.

To 10 ml. of the sample solution add 2 drops of the benzidine reagent. A blue color develops immediately. If a blue precipitate forms, the iridium concentration is too high. In this case, dilute the sample to a suitable concentration with the 0.1 per cent pure ammonium chloroplatinate solution.

Compare the color of the sample solution with that of the standard platinum solution similarly treated. Use a balancing type colorimeter. The quantity of iridium in the sample solution is then determined by reference to Table 34.

TABLE 34.

Height of 0.1 Per Cent Platinum Solution in mm.	Height of Sample Solution in mm.	Per Cent of Iridium in the Platinum
100	95 ± 1	0.05
100	90 ± 1	0.1
100	81 ± 1	0.2
100	74 ± 1	0.3
100	69 ± 1	0.4
100	65.5 ± 1.5	0.5

Detection of the platinum metals. Whitmore and Schneider[67] have studied the use of benzidine as a microchemical reagent for the platinum metals, and have recorded their results in Table 35.

TABLE 35.—REACTIONS OF BENZIDINE HYDROCHLORIDE WITH THE PLATINUM METALS

Reagent: Benzidine Hydrochloride—2.5 Per Cent Solution

Test Material	Description
$RuCl_3$	No apparent reaction.
$RhCl_3$	A very scant precipitate forms on standing.
$PdCl_2$	A dense, bright-yellow, amorphous precipitate forms immediately.
Na_2OsCl_6	Many long slender, bright-yellow, crystals develop immediately throughout the drop. These crystals grow to a very large size. All have ends cut at an angle to the long axis.
$IrCl_4$	A dense, bright-purple, amorphous precipitate forms immediately. This consists of a great many fine, slender, needle-shaped crystals forming an entangled mass over the drop.
H_2PtCl_6	A dense, white or very faintly yellow precipitate forms immediately. This consists of a great many fine, slender, needle-shaped crystals forming an entangled mass over the drop.
$AuCl_3$	A very dense, bright-blue, amorphous precipitate forms immediately. This is surrounded by a narrow border of a bright purple precipitate. At the edge of the blue zone some irregular crystalline structures develop.

The results given in this table were obtained by using a 2.5 per cent solution of benzidine hydrochloride with 1 per cent solutions of the materials to be tested.

Determination of mercury. Herzog[68] has prepared a number of complexes of the mercuric halides with benzidine by treating mercuric salts with a solution of benzidine in 50 per cent acetic acid. The formulas for the chloride, bromide and iodide respectively are: $[HgBzd]Cl_2$, $[HgBzd]Br_2$, $[HgBzd]I_2$.

Barcelo[7] has prepared the cyanide complex, $[HgBzd](CN)_2$. These salts are sufficiently characteristic and insoluble to be used for the quantitative determination of mercury. When aqueous and alcoholic solutions of any mercuric salts are treated with benzidine in slight excess, a precipitate is formed, and this may be washed with alcohol and ether, dried, and weighed. The gravimetric determinations based upon this method are reported as accurate as the standard sulfide method.[69]

A procedure based upon the formation of the insoluble complexes which benzidine forms with mercuric halides has also been used for the titrimetric determination of mercury.[70] An indirect method is based upon the following steps: the insoluble complex is formed in the usual manner; and, after filtering and washing, is dissolved in dilute hydrochloric acid. Benzidine is then precipitated as benzidine sulfate by means of sodium sulfate, and the precipitate is filtered from the solution. The precipitate and the filter are suspended in water in a beaker and titrated with 0.01 N sodium carbonate solution, using phenolphthalein as an indicator. One ml. of 0.01 N sodium carbonate solution = 0.01357 g. of $HgCl_2$ or 0.01002 g. of mercury. The average error reported with this method is less than 0.4 per cent.

Copper and mercury may be separated with the aid of benzidine, since the mercury complex is insoluble in dilute acetic acid, while the copper compound is soluble. After removing the mercury compound by filtration, the copper complex is precipitated by neutralizing the filtrate.[45]

Detection and determination of cadmium. Cadmium is precipitated in a neutral solution by adding a saturated solution of benzidine in 85 per cent alcohol. This precipitate may be weighed and used for the determination of cadmium.[45,233]

Detection of vanadium. Pentavalent vanadium may be detected by a color reaction based upon the oxidation of benzidine.[13,71] The following procedure is used:

Reagent. Dissolve 2 g. of benzidine in 100 ml. of ethyl alcohol at about 60° C., and add 100 ml. of water. Cool to about 30° C., and slowly add 100 ml. of phosphoric acid ($d = 1.70$) with stirring. Store the reddish colored reagent in a dark brown bottle and keep in a dark place.

Procedure. Mix 1 ml. of the above reagent with 2-3 ml. of phosphoric acid ($d = 1.70$), in a small test tube (155 × 14 mm.), cool to below 20° C., and while holding the tube vertically add the solution to be tested dropwise until a depth of about 4 mm. of the solution has been added. If the solution contains pentavalent vanadium, a yellow color appears. By this reaction as little as 0.4γ of vanadium can be detected, and the reaction is sensitive to 1:5,000,000.

This reaction is not specific, since chlorine, bromine, eerie and auric salts, chromates and permanganates give the test. The effect of chromate and manganate is eliminated by the use of Mohr's salt and sodium nitrite.[250] Since the test is due to the oxidation of benzidine, the color disappears on adding reducing agents such as ferrous sulfate or thiosulfates.

The following procedure is recommended for the detection of vanadium in alloy steel:[71]

Procedure. Dissolve 0.1 g. of the steel to be analyzed in 8 ml. of 6 N sulfuric acid, and oxidize the solution with 0.3 ml. of 7.5 N nitric acid. Evaporate the resulting solution to a thick mass, dilute with 75 ml. of water, and stir until a clear solution is obtained on warming. Cool to about 20° C. and test this solution with the reagent according to the procedure described above.

Hovorka[248] has prepared many derivatives of benzidine, and studied their reactions with vanadates.

Detection of silver. The ability of the silver ion to bring about the oxidation of benzidine, and its inability to oxidize the leuco compounds of the malachite green group of dyes, indicates that some activation is required for the oxidation process. A study conducted by Kul'berg and Serebryanyi[72] has shown that the reaction of benzidine with silver and the formation of $[AgBzd]NO_3$ is photochemical. The complex formed absorbs the lower part of the spectrum, thereby regenerating the sensitizer. In the succeeding stage the activated silver ion forms Ag_2O_2 with atmospheric oxygen, and this brings about the oxidation of the benzidine to the familiar blue compound. This reaction may be used for the detection of silver salts.[7,72]

Detection of phosphoric acid. Molybdates in solutions of mineral acids are converted into salts of the complex phosphomolybdic acid, $H_7[P(Mo_2O_7)_6]$, upon the addition of phosphates. The best known of these is perhaps the yellow ammonium salt, which, because of its slight solubility, is commonly used for the detection and determination of phosphoric acid. Arsenic and silicic acids react similarly with molybdates in acid solution to form arsenomolybdic acid, $H_7[As(Mo_2O_7)_6]$, and silicomolybdic acid, $H_8[Si(Mo_2O_7)_6]$. These three heteropoly acids are capable of oxidizing many inorganic and organic compounds which are effected only slightly, if at all, by free molybdic acid and molybdates. For example, iodides are only slightly oxidized by acid solutions of molybdates even at elevated temperatures, while phosphomolybdic acid liberates appreciable quantities of iodine even in cold solutions. This increased oxidizing power is apparently due to a special type of coordinated bonding of the molybdenum trioxide in the heteropoly acids of phosphorous, arsenic and silicon.

Benzidine is not oxidized by free molybdic acid nor by normal molybdates, but it is oxidized instantly to the blue meriquinoid oxidation product by phosphomolybdic acid, and also by an acetic acid solution of the ammonium salt. This reaction has been employed by Feigl[19,73-76,230,231] and by Frey[77] and by Dobbins and Kapp[78] as the basis for a test for phosphates. The reaction is extremely sensitive, since both of the products of this reaction are blue in color. One is the blue oxidation product of benzidine and the other is "molybdenum blue," which is obtained by reduction of molybdic acid. The test may be carried out as a test tube reaction or as a spot test.

Reagents. *Ammonia molybdate solution:* Dissolve 5 g. of ammonium molybdate in 100 ml. of cold water, and pour the resulting solution into 35 ml. of nitric acid ($d = 1.2$).

Benzidine solution: Dissolve 0.05 g. of benzidine or of benzidine hydrochloride in 10 ml. of concentrated acetic acid and dilute with water to 100 ml.

Procedure. Add 3 drops of the ammonium molybdate solution to 2 ml. of the solution to be tested, and add a few drops of the benzidine acetate solution. Then add 1 per cent ammonia solution until a permanent turbidity is formed. A blue coloration is obtained with as little as 0.00066 mg. of P_2O_5. If oxalates are present, more of the molybdate is required than is normally necessary. This is probably due to the formation of a complex oxalate-molybdate ion.

The above reaction may be modified and used as a spot test.

Reagents. Same as above.

Procedure. Place a drop of the solution to be tested on a strip of quantitative filter paper, and add a drop of the ammonium molybdate solution. Hold the paper over a beaker containing ammonium hydroxide. If phosphate is present, a blue stain appears on the paper when most of the free mineral acid is neutralized. The intensity of the color depends on the phosphoric acid content. By means of this test as little as 1.25γ of P_2O_5 can be detected at a concentration of 1:40,000.

Arsenates do not react under the conditions of the above test, since the formation of arsenomolybdic acid proceeds only very slowly in the cold. By the above procedure 1.5γ of phosphoric acid can be detected in the presence of 1000 times as much arsenic acid. With greater quantities of arsenic acid, any interference is eliminated by heating the test solution with a little sulfurous acid. The arsenious acid formed in this reaction does not react with molybdates. The excess sulfurous acid is removed by the addition of a solution of sodium nitrite to the acid solution to be tested.[79]

A more sensitive spot test is carried out as follows:

Reagents. Same as above.

Procedure. Place a drop of the ammonium molybdate solution on a piece of "blue band" filter paper (Schleicher & Schull No. 589) and dry in an air oven. Place a drop of the solution to be tested on the freshly prepared paper, and add a drop of the benzidine acetate solution and a drop of a saturated sodium acetate solution. A blue spot or ring is formed, depending upon the amount of phosphorus present. With this modification of the above spot test, as little as 0.05γ of P_2O_5 can be detected at a concentration of 1:1,000,000.

West and Houtman [80] have made a critical study of the interference with this test and report as follows:

(a) *Positive interference:* Beryllium, silicate, trivalent vanadium (color of ion), vanadate, arsenate (this reaction is much slower than the phosphate test), thiosulfate, chromic ion (color of ion), chromate (purple), selenite (slight), tellurite (slight), bromate (slight), iodide, ferrous iron, cyanide and ferricyanide.

(b) *Negative interference:* Fluorides.

(c) *Masking interference:* Bivalent copper (brown stain), trivalent gold (brown to blue stain), trivalent titanium (blue to black precipitate forms immediately upon addition to paper), stannous tin (same as titanium), nitrite (brown stain), trivalent antimony (causes immediate formation of blue stain in presence of phosphate), sulfide (black stain), permanganate (brown stain), ferric iron (color of ion), ferrocyanide (brown stain), trivalent ruthenium (color of ion), trivalent iridium (brown stain).

Soluble silicates interfere with the phosphate test since they also react with molybdic acid under the conditions of the above test to form a soluble silicomolybdic acid, which reacts with benzidine in much the same manner as phosphomolybdic acid to give a blue compound. It is possible, however, to detect phosphoric acid in the presence of both silicic and arsenic acids by preventing the formation of silicomolybdic and arsenomolybdic acids by the addition of tartaric acid. This depends upon the formation of a stable complex compound of molybdic and tartaric acids, which does not react with arsenic and silicic acids but which does react with phosphoric acid to form phosphomolybdic acid.[74] The test is carried out as follows:

Reagent. Dissolve 15 g. of tartaric acid in 100 ml. of the nitric acid-ammonium molybdate reagent used in above tests.

Bendizine solution: Same as used in above tests.

Procedure. Place a drop of the solution to be tested on a strip of filter paper and add a drop of the tartaric acid-molybdate solution, and hold the paper over a hot wire gauze. Then add a drop of the benzidine reagent, and hold the paper over a beaker containing ammonium hydroxide. A blue color is obtained with 1.5γ of P_2O_5 in the presence of 500 times as much silicic acid.

West and Houtman [80] have studied the ammonium molybdate-benzidine test for phosphates, and report that the use of tartaric acid to prevent the reaction with silicates and arsenates is impractical, since it also appears to inhibit the reaction with phosphates.

Determination of phosphate. Phosphate is quantitatively precipitated from neutral or dilute acetic acid solutions as benzidine phosphate by means of benzidine. This reaction has been used for the determination of phosphorus. The method is similar to that employed by Raschig [81,82] for the determination of sulfates (page 299). Phosphate is first separated as the benzidine salt, and this is filtered, washed, and titrated with a standard solution of a base.[83-85]

Procedure. Dissolve the sample containing approximately 0.1 g. of P_2O_5 in 50-150 ml. of water containing not more than 0.4 per cent of acetic acid. Pour this solution gradually and with vigorous stirring into a second solution prepared by diluting 30 ml. of 1 per cent benzidine solution, containing not more than 10 per cent acetic acid, to 150 ml. Allow the mixture to stand for 10-15 minutes and filter. Wash with water until the washings are no longer acid to litmus, and transfer the precipitate and paper to a 500-ml. flask containing carbon dioxide-free distilled water. Carefully titrate with 0.1 N sodium hydroxide, using phenolphthalein as the indicator. The number of ml. of the base used multiplied by 0.00355 gives the number of grams of P_2O_5 contained in the sample used.

Phosphorus may be determined in the presence of sulfates, as in the analysis of "super-phosphates," by utilizing the fact that benzidine phosphate, unlike benzidine sulfate, dissolves in dilute hydrochloric acid. Both the phosphate and the sulfate are precipitated with benzidine, and the washed precipitate is treated with hydrochloric acid to dissolve benzidine phosphate. Benzidine phosphate is reprecipitated after filtering by making the filtrate alkaline with ammonium hydroxide. Sulfate may be removed more conveniently by precipitation as barium sulfate.

Arnold[86] attempted to use benzidine for the separation of phosphoric and tungstic acids, but reports that no satisfactory procedure was developed. Markova[87] has used the phosphomolybdic acid-benzidine reaction for the colorimetric determination of small quantities of phosphorus in minerals.

Reagents. *Benzidine reagent:* Dissolve 0.25 g. of benzidine hydrochloride in 5 ml. of 33 per cent acetic acid and sufficient water to make 100 ml. of solution.

Ammonium citrate solution: Mix 50 g. of citric acid and 63 ml. of 25 per cent ammonia solution, and add sufficient water to make 100 ml. of solution.

Ammonium molybdate solution: Dissolve 15 g. of $(NH_4)_6Mo_7O_{24}$ in 100 ml. of water, and pour this solution slowly into 100 ml. of 6 N nitric acid.

Procedure. Treat 5 g. of the mineral with 40 ml. of aqua regia for 30 minutes, and dilute the mixture to 250 ml. Mix well, transfer a 5-ml. aliquot to a 100-ml. volumetric flask, and dilute to the mark. Treat 10 ml. of the diluted solution with 4 drops of the ammonium citrate solution, 5 drops of the ammonium molybdate solution, and 4 drops of benzidine solution. Compare the resulting color with that obtained by treating in a similar manner standards containing approximately the same amount of phosphorus.

The standard solution is prepared as follows: dry monopotassium phosphate for several days in a desiccator over sulfuric acid. Dissolve 0.4394 g. of the salt in water, add 10 ml. of 1:3 sulfuric acid and dilute to 1 liter. This solution contains 0.1 mg. of phosphorus per ml., or 0.229 mg. of P_2O_5. This solution may be diluted if necessary.

A yellow precipitate of $(Bzd)_3(H_3PO_4)_2(MoO_3)_{24} \cdot 22H_2O$ is formed when 20 ml. of a 10 per cent ammonium molybdate solution and 20 ml. of a 1 per cent benzidine hydrochloride solution are added to 100 ml. of a 0.75 N hydrochloric acid solution containing 0.2-1.5 mg. of phosphorus. This precipitate dissolves in 15 ml. of 2 per cent hydrazine sulfate solution to yield a blue color which may be used for the estimation of the phosphorus content after precipitating insoluble benzidine sulfate. The precipitate is washed with 0.025 N hydrochloric acid, and flocculation is aided by the addition of 2 g. of sodium chloride.[88]

Detection and determination of silicic acid. Soluble silicates react with an acid solution of ammonium molybdate to form a complex silicomolybdate, $H_4SiO_4 \cdot 12MoO_3 \cdot xH_2O$. The ammonium salt of this acid differs from those of the analogous phosphoric acid and arsenic acid compounds in that it dissolves in water and acids to form a yellow solution. This reaction was first used by Jolles and Neurath [89] for the detection of silicic acid in water. Silicomolybdic acid, like the corresponding phosphomolybdic acid, is capable of oxidizing benzidine in an acetic acid solution to a blue product, and simultaneously the blue lower oxides of molybdenum are formed. A sensitive test for silicic acid is based upon this reaction.[90-92] The formation of silicomolybdic acid occurs rather slowly and incompletely at low temperatures, but if the reaction mixture is gently warmed in a small crucible or on filter paper, the reaction proceeds rapidly and completely.

Reagent. *Ammonium molybdate solution:* Dissolve 5 g. of ammonium molybdate in 100 ml. of cold water and pour into 35 ml. of nitric acid ($d = 1.2$).

Procedure. Add 2 drops of the ammonium molybdate reagent to 1 ml. of a dilute hydrochloric or nitric acid solution of the material to be tested. The acidity of this solution should not be greater than 0.5 N. Heat to boiling and allow to cool. Add 1-2 drops of 0.25 per cent solution of benzidine in 10 per cent acetic acid and an equal volume of a saturated solution of sodium acetate. A blue color or precipitate is formed if silicic acid is present.

This test may also be carried out by means of a spot test or a drop reaction:

Reagents. *Ammonium molybdate solution:* Dissolve 5 g. of ammonium molybdate in 100 ml. of cold water and pour into 35 ml. of nitric acid ($d = 1.2$).

Benzidine solution: Dissolve 0.05 g. of benzidine or benzidine hydrochloride in 10 ml. of concentrated acetic acid and dilute with water to 100 ml.

Procedure. Place a drop of the solution to be tested and a drop of the molybdate reagent on a strip of filter paper and warm gently over a wire gauze. Then add a drop of the benzidine solution and hold the paper over a bottle of ammonium hydroxide. A blue color forms if silicic acid is present. In this way 1γ of SiO_2 can be detected at a concentration limit of 1:50,000.

The test is carried out in a porcelain crucible as follows:

Procedure. Place a drop of the slightly acid solution to be tested in a porcelain crucible and mix with a drop of the molybdate solution. The acidity of the solution to be tested should not exceed 0.5 N. Carefully warm the crucible and contents over a wire gauze until bubbles form, and then cool. Add a drop of the benzidine solution and a drop of a saturated solution of sodium acetate. By employing this procedure, the test is made about 10 times as sensitive as by the spot method.

The crucible should be tested for resistance to solution before it is used. This test may be carried out as follows: Place a drop of water and a drop of the molybdate solution in the crucible, mix, warm, and treat as above. If a trace of blue color forms on addition of benzidine solution and sodium acetate, do not use the crucible for the silicic acid test. It is necessary to heat the reaction mixture to hasten and complete the formation of the silicomolybdic acid; when this test is carried out in a crucible, care must be taken to avoid boiling the mixture, since this might cause traces of silicic acid to dissolve from the porcelain and interfere with the test.

Since phosphoric acid reacts with ammonium molybdate to yield a compound which also gives a blue color with benzidine, the test for silicic acid must be carried out in the absence of phosphoric acid. This separation is accomplished by precipitating phosphoric acid with ammonium molybdate and applying the benzidine test to the filtrate after the removal of the insoluble phosphomolybdate. The test for silicic acid is made more positive by the addition of oxalic acid. This causes the decomposition of small quantities of ammonium phosphomolybdate while silicomolybdic acid is stable toward oxalic acid. The following procedure is used for the detection of silicic acid in the presence of phosphoric acid:

Procedure. Place a drop of a solution to be tested, which should not contain more than 0.1 mg. of phosphate, in a microcentrifuge tube and add 2 drops of the ammonium molybdate solution used in the above tests. Centrifuge, and transfer the clear supernatant liquid to a microcrucible and warm gently. Allow to cool. Add 2 drops of a 1 per cent solution of oxalic acid to decompose the last traces of ammonium phosphomolybdate, and add 1 drop of an acetic acid solution of benzidine, and a few drops of a saturated solution of sodium acetate. The usual blue color is obtained if silicic acid is present. By this procedure 6γ of SiO_2 can be detected in the presence of 1.5 mg. of P_2O_5.

Feigl and Leitmeier[93] have used the benzidine-molybdic acid test to detect silica in minerals, and Thanheiser[92] has used a similar reaction to detect silicon in steel. This method may also be applied to the detection of silicic acid in limestone, dolomite and cement.[94]

Detection of germanium. Germanates, in solutions of mineral acids, react with molybdates to form insoluble germanomolybdic acid $H_8[Ge(Mo_2O_7)_6]$. This compound like similar complex compounds of arsenic, phosphorous and silicon with molybdic acid is capable of oxidizing a number of organic and inorganic compounds. When benzidine is treated with germanomolybdic acid in an acid solution which is buffered with ammonium or sodium acetate, a blue color appears due to the formation of the lower oxides of molybdenum and the oxidation product of benzidine. If conditions are properly controlled, this reaction serves as a sensitive test for germanium.[95]

Procedure. Place a drop of an alkaline or slightly acid solution to be tested on a spot plate, or on a strip of filter paper, and add 1 drop of a solution prepared by dissolving 1.5 g. of ammonium molybdate in 10 ml. of water and 10 ml. of concentrated nitric acid. Then add a drop of 0.1 per cent solution of benzidine in acetic acid. Finally add a little saturated sodium acetate solution or expose the drop to ammonia vapors. A blue color is obtained with as little as 0.25γ germanium.

A number of substances interfere with this reaction. Reducing agents which reduce molybdates directly, such as stannous and ferrous salts, arsenites and tetravalent selenium compounds must be absent. Arsenic acid, phosphoric acid and silicic acid interfere since they also form heteropoly acids of molybdenum which react with benzidine. In the presence of these substances, germanium is removed by distilling volatile germanium tetrachloride from a solution that is 3.5-4.0 N in hydrochloric acid. The molybdate-benzidine test is applied to the distillate. The distillation of germanium from the hydrochloric acid solution does not yield a complete separation from all interfering substances, since both trivalent arsenic and tetravalent selenium are also carried over into the distillate, and these substances materially reduce the sensitivity of the germanium test. Pentavalent arsenic, if present, may eventually interfere with the detection of germanium, since by boiling in an acid solution it may be reduced to trivalent arsenic and pass over as volatile arsenic trichloride. In order to test for germanium in the presence of selenium and arsenic, it is best to convert these elements to the higher oxides by evaporating with a 30 per cent solution of hydrogen peroxide and 1 or 2 drops of ammonium hydroxide. The dry residue is then treated with a crystal of potassium permanganate and 2 drops of 4 N hydrochloric acid. Germanium is distilled and the test applied to a drop of the distillate. Any free chlorine which may be present is destroyed by the addition of a drop of 5 per cent sodium sulfite solution after the addition of the molybdate reagent. By using this procedure, 10γ of germanium may be detected in the presence of 1000 times as much selenium, or 800 times as much arsenic.[96]

Detection of sulfate. When a solution of sulfuric acid or a sulfate is treated with benzidine and formaldehyde, especially in the presence of copper or manganese salts, an orange sulfate crystallizes in the form of hexagonal plates. This reaction has been used by Pozzi-Escot[97,240] for the microchemical detection of sulfates.

Titrimetric determination of sulfate. Benzidine is a weak organic base, and forms stable salts with the strong mineral acids. The sulfate is of particular interest because of its slight solubility in water, and particularly in water containing hydrochloric acid. Since benzidine is such a weak base, aqueous solutions of its salts undergo complete hydrolysis. Benzidine hydrochloride is decomposed according to the equation

$$C_{12}H_8(NH_2)_2 \cdot 2HCl + 2H_2O \rightleftarrows C_{12}H_8(NH_2)_2(H_2O)_2 + 2HCl$$

into hydrochloric acid and benzidine hydroxide; and the latter further decomposes into benzidine and water. In other words, an aqueous solution of benzidine hydrochloride behaves like a mixture of hydrochloric acid and benzidine. Since the free base is neutral toward phenolphthalein, the amount of acid formed by the hydrolysis of a benzidine salt may be determined by titration with a standard alkali, using phenolphthalein as an indicator. Two methods have been used for the titrimetric determination of sulfuric acid by means of benzidine. In the first method, originally proposed by Muller,[98-100] the neutral solution of the sulfate is treated with a solution of benzidine hydrochloride of known acidity, and the sulfate precipitated according to the following equation:

$$C_{12}H_8(NH_2)_2 \cdot 2HCl + SO_4^{=} \rightarrow C_{12}H_8(NH_2)_2 \cdot H_2SO_4 + 2Cl^-$$

The precipitate of benzidine sulfate is removed by filtration, and the filtrate is titrated with a standard solution of an alkali. The loss in acidity corresponds to the amount of sulfuric acid present.

The second method, which is the most frequently employed in the determination of sulfates, was proposed by Raschig.[81,82] By this method the neutral or acid solution containing the sulfate is treated with a solution of benzidine hydrochloride, and the precipitate of benzidine sulfate removed by filtration. It is then washed, and suspended in water, and finally titrated with 0.1 N sodium hydroxide at 50° C. This method has been studied extensively by numerous investigators, and now constitutes one of the most important procedures for determining sulfur in organic as well as inorganic substances.[102-112,252]

The following procedure is based upon the method originally proposed by Raschig.[81,82]

Reagent. Mix 40 g. of benzidine with 40 ml. of water, and rinse the resulting mixture into a liter volumetric flask with the aid of 750 ml. of water. Add 50 ml. of concentrated hydrochloric acid and dilute to the mark. Shake well until the solid is dissolved, and filter if necessary. This solution is used as a stock reagent. When ready for use in the determination of sulfate, dilute 10 ml. with 190 ml. of water.

Procedure. To the neutral or slightly acid solution containing not more than 0.1 g. of sulfate per 50 ml. of solution, add the diluted benzidine solution, using 150 ml. for each 0.1 g. of sulfate ion. Allow the mixture to stand for 5 minutes, and filter through a funnel prepared as follows: Place a perforated porcelain plate, having a diameter of about 40 mm. at the top, in a 200-ml. funnel; and then place two pieces of filter paper having a diameter of about 46 mm. on this plate. Insert the funnel in a rubber stopper and place in a suction flask. Moisten the filter with water and apply gentle suction, and then press this paper to the sides of the funnel so that a tight pad is formed about 3 mm. in depth. Pour the supernatant liquid through this filter, and rinse the precipitate and mother liquor into the funnel, and allow to drain. Wash the precipitate with 15 ml. of water, added in small portions. Remove the filter from the funnel and the porcelain plate, and place the precipitate and the filter in an Erlenmeyer flask. Add 50 ml. of water and shake the contents of the stoppered flask until a homogenous paste is formed. Remove the stopper from the flask, rinse off with water, add a drop of phenolphthalein indicator solution, heat to about 50° C., and titrate with 0.1 N sodium hydroxide. When the end-point is nearly attained, boil the solution for 5 minutes, and then finish the titration.

$$\text{One liter of 0.1 N NaOH} = \frac{H_2SO_4}{20} = 4.904 \text{ g. } H_2SO_4.$$

This method does not give reliable results in the presence of ferric salts, but this interference is eliminated by reducing the ferric ion with hydrazine hydrochloride. There should not be more than 10 moles of hydrochloric acid, 15 moles of nitric acid, 20 moles of acetic acid, 5 moles of alkali salt or 2 moles of ferric iron to 1 mole of sulfuric acid.

Chromates interfere with the precipitation of sulfates by oxidizing the benzidine reagent. Knorre[113] has found that this oxidation can be prevented by the use of hydroxylamine hydrochloride, but that attempts to use this method for the determination of sulfates in the presence of chromates give high results. By the addition of a few ml. of N hydrochloric acid, however, very close results are obtained. There is also some difficulty in the precipitation of sulfates with benzidine when the solution is boiled, due to the formation of complex chromium compounds, but this is overcome by boiling with sodium or ammonium acetate before precipitating the sulfate with benzidine.

Sulfate is determined in the presence of lead, as in the analysis of lead sulfate, by dissolving the sample in ammonium acetate solution. The solution is poured into an excess of dilute benzidine hydrochloride solution, filtered, the precipitate washed with a very little 24 per cent alcohol, and then titrated with 0.1 N potassium hydroxide, using phenolphthalein as an indicator.[114]

In the control of production of sulfuric acid by the chamber process, a measured volume of tower gases, which contains sulfur dioxide and oxides of nitrogen, is oxidized in an aqueous solution with neutralized hydrogen peroxide, and the total acid is then titrated with 0.1 N sodium hydroxide solution, using methyl orange as an indicator. The sulfate is precipitated with benzidine hydrochloride solution, and the resulting benzidine sulfate is titrated with sodium hydroxide in the usual manner.[115,116]

TABLE 36.—SOLUBILITY OF BENZIDINE SULFATE

Normality of Hydrochloric Acid Solution	Solubility of Benzidine Sulfate in grams per 1000 g. of Solution	Solubility of Benzidine Hydrochloride in grams per 1000 g. of Solution
0.000	0.098	5.346
0.239	0.542	....
0.530	0.942	....
1.009	1.253	....
2.074	1.790	....
2.825	1.930	....
2.884	....	2.172
4.139	1.887	....
5.607	....	1.246
5.622	1.774	....
7.601	1.544	....
9.942	1.499	....
9.870	....	1.224
11.099	1.490	....

TABLE 37.—EFFECT OF pH ON PRECIPITATION OF BENZIDINE SULFATE

Vol. Na_2SO_4 Soln. ml.	M NaAc ml.	M HAc ml.	Vol. H_2O ml.	Vol. Reagent ml. (8 g./l.)	mg. S Present	mg. S Found	Per Cent Error	pH of Filtrate
20	5.6	2.4	12	20	13.35	12.99	3.1	4.7
20	5.6	2.4	12	20	13.35	13.02		4.7
20	3.2	4.8	12	20	13.35	13.04	2.5	4.1
20	3.2	4.8	12	20	13.35	13.20		4.2
20	1.6	6.4	12	20	13.35	13.46	0.5	3.6
20	1.6	6.4	12	20	13.35	13.28		3.6
20	0.2	7.8	12	20	13.35	13.36	0	2.15
20	0.2	7.8	12	20	13.35	13.33		2.15
20	...	...	20	20	13.35	13.28	0	2.0
20	...	...	20	20	13.35	13.36		2.0
	N HCl ml.							
20	4	...	16	20	13.35	13.22	0.5	1.25
20	4	...	16	20	13.35	13.38		1.25
20	8	...	12	20	13.35	13.06	2.0	0.94
20	8	...	12	20	13.35	13.12		0.96
					13.35			

The present difficulties in the use of the benzidine method for sulfuric acid arise in obtaining conditions necessary for the maximum precipitation of benzidine sulfate. The solubility of benzidine sulfates in hydrochloric acid may cause considerable error in the determination unless the acid concentration is kept quite low. Meldrum and Newlin [117] and Bisson and Christie [118] have determined the solubility of benzidine sulfate in water and hydrochloric acid at various concentrations, and the results are shown in Table 36, which is taken from the work of Meldrum and Newlin.

It is obvious that in order to secure complete precipitation, the acidity of the solution from which the precipitation is to take place must be carefully adjusted. Owen [119] has studied the effect of pH upon the precipitation of benzidine sulfate and the results of his investigations are given in Table 37.

According to Owen,[119] benzidine sulfate should be precipitated at a pH of 2.75 ± 0.3.

The presence of chlorides may also cause some error in the determination of sulfates by the benzidine method by increasing the solubility of benzidine sulfate. The effect of chlorides is shown in Table 38, which is taken from the work of Owen.[119]

TABLE 38.—EFFECT OF CHLORIDES UPON THE DETERMINATION OF SULFUR BY THE BENZIDINE METHOD

Vol. Soln. ml.	S Present mg.	Cl Present mg.	Cl:S Ratio	Vol. Reagent (8 g./l.)	S Found mg.
20	6.67	0	0	10	6.66
20	6.67	0	0	10	6.68
20	6.67	243	36.4	10	6.66
20	6.67	243	36.4	10	6.65
20	6.67	61	9.1	10	6.63
20	6.67	61	9.1	10	6.66
40	3.36	0	0	5	3.22
40	3.36	0	0	5	3.22
40	3.36	122	36.3	5	3.12
40	3.36	122	36.3	5	3.06
40	3.36	486	145	5	2.88
40	3.36	486	145	5	2.82

In the analysis of urine and other biological fluids, phosphate is the greatest source of error. This is of course also true of all solutions containing soluble phosphates. A number of investigators who have used this method claim that the precipitation of benzidine phosphate is prevented by adjusting the acidity of the solution to pH 2 [81,82,107,120-124] before precipitating with benzidine. On the other hand, many procedures provide for the removal of the phosphate before precipitating the sulfate with benzidine.[125-134]

The effect of phosphates upon the determination of sulfates is shown in Table 39, taken from the work of Owen.[119]

TABLE 39.—EFFECT OF PHOSPHATE ON DETERMINATION OF SULFATE

Vol. of Soln. ml.	Vol. 2.5 N HCl Added ml.	Vol. Reagent (8 g./l) ml.	mg. S Present	mg. S Found	Per Cent Error	mg. P in ppt.	pH of Filtrate
40	None	20	13.36	14.09	+5.4	0.48	1.9
40	None	20	13.36	14.09	+5.4	0.34	1.9
40	None	20	13.36	14	+4.5	0.40	1.9
40	None	20	13.36	13.96	+4.2	0.36	1.9
40	None	20	13.36	14.09	+5.4	0.48	1.9
40	None	20	13.36	14.20	+6.0	....	....
40	None	20	13.36	13.89	+3.7	....	....
38.4	1.6	20	13.36	13.11	—1.9	....	1.1
38.4	1.6	20	13.36	12.96	—3.0	....	1.1

At pH 1.9, phosphate causes an error of 4-6 per cent, and with greater hydrochloric acid concentration the sulfate is only incompletely precipitated. Consequently, it appears preferable to remove phosphates before precipitating sulfate with benzidine.

In addition to proper acidity, the time of standing before filtration, and variations in temperature exercise marked effect upon the precipitation of benzidine phosphate. For example, error due to phosphate is greatly increased when the mixture is allowed to stand for 24-48 hours, while at lower temperatures greater quantities of phosphates are precipitated.

Two methods have been proposed for the removal of phosphates from serum: Fiske [125] recommends precipitating phosphate as magnesium ammonium phosphate, while Yoshimatsu [128] claims good results by precipitating with uranyl acetate in the presence of an acetate buffer at pH 5. Both methods give good results.

A number of investigators have applied the benzidine method to the determination of sulfur in urine.[121,122,124,125,135-138,251] The following method is recommended by Fiske: [125]

Procedure. *Removal of phosphate:* Transfer to a 50-ml. volumetric flask sufficient urine to contain 5-10 mg. of sulfur as inorganic sulfate, and dilute to 25 ml. with water. Add 1 drop of phenolphthalein indicator, and 1 drop of concentrated ammonium hydroxide, or as much as is necessary to make the solution faintly pink. Then add 5 ml. of 5 per cent ammonium chloride solution and dilute to the mark. Mix well and pour the solution into a dry Erlenmeyer flask containing 0.65 g. of finely powdered basic magnesium carbonate. Shake for 1 minute and transfer enough of the suspension to a 9-cm. filter paper to fill it almost to the top. Allow the filtrate to drain back into the Erlenmeyer flask, and then filter the entire suspension through the same paper into a dry container. The filtrate is free from phosphate and may be used for the determination of sulfur by the benzidine method.

Determination of inorganic sulfate. Use 5 ml. of the filtrate from the above procedure, precipitate with benzidine hydrochloride solution, and titrate the precipitate with sodium hydroxide in the usual manner.

The benzidine method has been successfully applied to the determination of sulfates in blood and other biological liquids.[129-131,139-141] Proteins are first precipitated, and then sulfate is precipitated from the resulting filtrate in the usual manner. The following procedure for preparing the blood serum has been used by Power and Wakefield.[132]

Procedure. Mix 2 ml. of serum and 2 ml. of 20 per cent trichloroacetic acid in a centrifuge tube and allow to stand for 30 minutes. Centrifuge the precipitated proteins, and filter off the supernatant liquid. Mix 2 ml. of the filtrate in a centrifuge tube with 5 ml. of a 1 per cent acetone solution of benzidine, and allow the mixture to stand for 4 hours. Centrifuge, and carefully pour off the supernatant liquid without disturbing the precipitate. Wash once with acetone, centrifuge and pour off the supernatant liquid. The precipitate may be titrated in the usual manner with sodium hydroxide, or it may be determined by oxidizing with potassium permanganate or potassium dichromate.

The benzidine method for sulfates has also been successfully applied to the determination of sulfur in iron pyrites,[142,145] coal and coke,[146,148] fertilizers,[149] soil extracts,[150] water,[150] gases from the roasting of ores,[151] portland cement,[152] rubber,[153] sulfide and thiosulfate liquors [154] and novoarsenobenzene.[155]

A number of other titration methods have been proposed which do not depend upon the titration of precipitated benzidine sulfate with a standard solution of a base. Testoni [156] has proposed the titration of a solution of sulfate with a standard solution of benzidine acetate, using filter paper moistened with lead peroxide as an indicator. This test paper gives a purple color with 1 part of benzidine in 200,000 parts of solution. The standard benzidine solution is prepared as follows:

Procedure. Dissolve 10 g. of benzidine in 100 ml. of glacial acetic acid and dilute with water to 1 liter. Allow to stand for 24 hours and filter. Titrate the filtrate with standard 0.1 N sulfuric acid to determine the sulfate equivalent of the benzidine solution. The end-point is determined by titrating the sulfate solution, filtering, and testing the filtrate for an excess of benzidine by means of lead peroxide paper. When two titrations are made, using amounts of reagent differing by 0.1 ml., in which the filtrate from one shows an excess of the reagent, while the filtrate from the second shows none, the average of the two results is taken as the correct standard value.

The same procedure is employed for determining sulfate in an unknown solution as is used in the standardization of the benzidine solution.

Chromates and other oxidizing agents must be reduced before carrying out this determination and ferric salts must be removed. The sulfate solution must be slightly acid with acetic acid, since free mineral acids prevent an accurate determination of the end-point. The use of acetic acid also prevents the occlusion of benzidine in the precipitate, as is the case when hydrochloric acid is used. This method is rapid, and is accurate to within 1 per cent of the true value.

Antanasiu and Velculescu [157] have attempted to titrate sulfates potentiometrically with a standard solution of benzidine, but have been unsuccessful in developing a satisfactory procedure. If a known excess of benzidine is added to a solution containing sulfate, and the excess reagent titrated with potassium nitrite solution, excellent results are obtained.

Jarvinen [120] used benzidine for the precipitation of sulfates, but for the final determination dissolved the precipitate in hydrochloric acid and precipitated the sulfate with barium chloride.

Ollgaard [134] determined sulfates in serum by precipitating with benzidine, and then titrating the benzidine sulfate with standard barium chloride solution, using rhodizonic acid as the indicator.

Savich [158] has used benzidine for the conductometric titration of sulfuric acid in a mixture of sulfuric and nitric acids. The mixture is first neutralized with sodium or potassium hydroxide, and is then titrated with benzidine hydrochloride solution. The electrical conductivity decreases until all sulfuric acid is converted to benzidine sulfate, whereupon it undergoes a sudden change. The benzidine hydrochloride solution should have a concentration of approximately 1 per cent. Best results are obtained when the solution is about 0.1 N in nitric and sulfuric acids.

Another titrimetric procedure for the determination of sulfate with benzidine is based upon the precipitation of sulfate as benzidine sulfate, followed by the oxidation of benzidine with standard potassium permanganate or potassium dichromate solutions. Raiziss and Dubin [123] have recommended the direct titration of benzidine sulfate with potassium permanganate solution, but the end-point is not sharp.[124] This method has been modified by Hibbard [159] who recommends the use of a measured excess of potassium permanganate and the treatment of the excess with standard oxalic acid.

Procedure. The unknown solution should be free from iron, heavy metals, nitrates, phosphates and organic matter. To 10-25 ml. of this solution, containing between 0.5 and 4.0 mg. of sulfate, add 1 drop of phenolphthalein solution and dilute hydroxide solution until the mixture is just alkaline. Carefully neutralize with 0.1 N hydrochloric acid, and then add an excess of 0.1 ml. of acid for each 5 ml. of solution. Cool the solution, and add 5 ml. of 0.8 per cent benzidine hydrochloride solution and allow to stand for 15-30 minutes. Filter through a Gooch crucible. Rinse the flask 3 times with 5-ml. portions of cold water, and wash the inside of the crucible once. Transfer the precipitate, along with the asbestos pad, to the flask in which the precipitation was carried out and heat with 1 ml. of 10 per cent sodium hydroxide in a boiling water-bath for a few minutes. Add 10 ml. of 1:1 sulfuric acid, and dilute with hot water to a volume of 100 ml. Run in from a buret, 0.05 N potassium permanganate solution until there is an excess of 5 ml. Heat the solution on a water-bath for exactly 10 minutes. Add 10 ml. of 0.05 N oxalic acid and complete the titration with 0.05 N potassium permanganate solution. Better results are obtained by running a blank determination. One ml. of 0.05 N potassium permanganate is equivalent to 0.12 mg. of sulfate.

Marsden and Pollard [160] have used a similar method for the microchemical determination of sulfates in soil and soil extracts. Conditions must be carefully controlled for accurate results. In this procedure, sulfate is precipitated with benzidine in the usual manner, and the benzidine in the precipitate is titrated as follows:

Procedure. Dissolve the precipitate from 0.05-2.0 mg. of sulfate in 5 ml. of 0.5 per cent potassium hydroxide solution. Transfer the solution to a 100-ml. Erlenmeyer flask, and rinse the vessel four times with 5 ml. of water and collect the washing in the flask. Add 1 ml. of concentrated sulfuric acid and place on a steam-bath. When hot, run in 0.05 N potassium permanganate solution to an apparent end-point, and then add an excess of one-fourth of the volume of the permanganate used plus an additional 1 ml. of the solution. Again place the flask on the steam-bath for 10 minutes, add 2 ml. of 0.05 N sodium oxalate solution, and when the precipitated manganese has dissolved, complete the titration with the standard potassium permanganate solution. The number of ml. of 0.05 N potassium permanganate, less 2, multiplied by 0.118 gives the number of mg. of sulfate present.

Power and Wakefield[182] used a similar method for the determination of inorganic sulfate in blood serum, but they used potassium dichromate as the oxidizing agent.

Procedure. Mix 2 ml. of serum and 2 ml. of 20 per cent trichloroacetic acid in a centrifuge tube, and allow to stand for 30 minutes. Centrifuge the precipitated serum proteins, and filter the supernatant liquid. Mix 2 ml. of the filtrate in a centrifuge tube with 5 ml. of a 1 per cent acetone solution of benzidine. Allow the mixture to stand for 4 hours, centrifuge, and carefully pour off the supernatant liquid without disturbing the precipitate. Wash the precipitate once with acetone, centrifuge, pour off the wash liquid, and heat the residue to 80° C. in an oven. Oxidize the dried benzidine sulfate quantitatively by adding a carefully measured excess of standard potassium dichromate and concentrated sulfuric acid. The oxidation proceeds smoothly and gives carbon dioxide ammonia and water. One mole of benzidine = 9 moles, or 54 equivalents, of dichromate. The benzidine combined with 1 mg. of sulfate requires for its oxidation 56.25 ml. of 0.01 N potassium dichromate solution. Determine the excess dichromate by an iodometric determination. Results are made more accurate by means of a blank determination.

Results obtained in the determination of 3-5 mg. of sulfate in 100 ml. of solution are about 95-100 per cent accurate.

Sulfate has been determined indirectly by an interesting method proposed by Hoagland.[234] This method is based on the combustion of the carbon contained in the precipitate of benzidine sulfate, and the measurement of the volume of carbon dioxide formed. For quantities of sulfur of 0.04 mg. and greater, the average deviation is 0.5 per cent. The average error is only 2 per cent for 0.02-0.04 mg. of sulfur.

Colorimetric determination of sulfate. Kahn and Leiboff[161] have used benzidine for the colorimetric determination of sulfates. After precipitation as benzidine sulfate, the benzidine in the precipitate is diazotized with nitrous acid, and the resulting diazo compound is coupled with phenol in an alkaline solution. This causes a yellow color, the intensity of which is proportional to the amount of benzidine present. The color produced in this reaction is due to the formation of a simple tetrazo dye according to the following series of changes:

$$H_2N—C_6H_4—C_6H_4—NH_2 + 2HNO_2 + 2HCl \rightarrow (C_6H_4—N{=}N—Cl)_2 + 4H_2O$$

$$(C_6H_4—N{=}N—Cl)_2 + 2C_6H_5ONa + 2NaOH \rightarrow$$
$$(C_6H_4—N{=}N—C_6H_4ONa)_2 + 2NaCl + 2H_2O$$

Reagents. *Benzidine hydrochloride:* Place 4 g. of pure benzidine hydrochloride and 10 ml. of hydrochloric acid in a 500-ml. cylinder and dilute with water to 500 ml. Mix until all the solid has dissolved and filter. If the solution is brown, decolorize by shaking with animal charcoal and allowing to stand for a few hours before filtration.

Sodium phenolate: Dissolve 50 g. of phenol crystals in about 500 ml. of water and add 15 per cent sodium hydroxide solution until the mixture is alkaline to litmus. Dilute with water to 1 liter.

Standard ammonium sulfate solution: Weigh accurately 4.1216 g. of pure dry ammonium sulfate and dissolve in water in a 1-liter volumetric flask, and dilute to the mark. One ml. of this solution contains 1 mg. of sulfur. The standards used in the determination contain 0.1 mg. of sulfur in 2 ml. This solution is prepared by diluting the stock solution 1:20. Preserve with chloroform.

Procedure. Kahn and Leiboff originally developed this method for the determination of inorganic sulfates in urine. Precipitate sulfate in the usual manner from 5 ml. of urine that has been diluted with an equal volume of water. Then filter, wash, and treat as follows: Add to the precipitate in a centrifuge tube 0.5 ml. of concentrated hydrochloric acid and 5 ml. of distilled water in small portions, shaking the tube after each addition. Add 1 ml. of 10 per cent sodium nitrite solution and allow the mixture to stand for 5 minutes.

Measure accurately 2 ml. of standard ammonium sulfate solution into a clean centrifuge tube, and add 2 ml. of the benzidine reagent and 4 ml. of 95 per cent alcohol. Allow to stand for 15 minutes and centrifuge. Pour off the supernatant liquid and wash twice with 50 per cent alcohol. Diazotize the resulting precipitate with 0.5 ml. of concentrated hydrochloric acid, 5 ml. of water, and 1 ml. of sodium nitrite in the same manner used for the unknown. Allow the mixture to stand 5 minutes and transfer the unknown and standard to separate 100-ml. cylinders. Rinse the centrifuge tubes twice with 10-ml. portions of water and add the washings to the respective cylinders.

To each cylinder add 5 ml. of 15 per cent sodium hydroxide and 5 ml. of sodium phenolate and dilute to 100 ml. Compare the resulting solutions in a colorimeter with the standard set at 20 mm. If the color is too deep, dilute an aliquot part of the unknown solution. The quantity of sulfur is calculated from the following equation:

$$\frac{S}{R} \times 0.1 \times \frac{DR}{DS} \times 100 = \text{mg. } S \text{ in 100 ml. urine}$$

S = reading of the standard
R = reading of the unknown
DR = dilution of the unknown
DS = dilution of the standard

Babkin[162] has used the method of Kahn and Leiboff, but claims that results are not satisfactory. He has compared the results obtained using the colorimetric method with those employing a gravimetric procedure, and has found a discrepancy of as much as 50 per cent. It seems likely, however, that in view of the limitations of the gravimetric method, this is not a sufficient justification for condemning the colorimetric procedure.

Cuthbertson and Tompsett[163] have used a similar procedure but have substituted thymol for phenol as the coupling agent.

Klein[253] used N-(1-naphthyl)ethylenediamine dihydrochloride as the coupling agent. For details of this procedure, see section on N-(1-naphthyl)ethylenediamine.

Hubbard[126,127] has based a determination of sulfate upon the color formed when a precipitate of benzidine sulfate is treated with hydrogen peroxide and ferric chloride. The following procedure is used for determining sulfates in blood serum:

Reagents. *Benzidine solution:* Dissolve 4.015 g. of benzidine hydrochloride in sufficient water to make a liter of solution. One ml. of this solution is equivalent to 0.5 mg. of sulfur.

Hydrogen peroxide solution: Dilute U.S.P. 3 per cent hydrogen peroxide with 9 parts of distilled water. Do not use hydrogen peroxide from a bottle that has been opened for any length of time.

Procedure. Precipitate benzidine sulfate from 1 ml. of filtered, protein-free serum in the usual manner. Wash, and to the precipitate add 2 ml. of 0.2 N hydrochloric acid and warm. If the precipitate does not dissolve add 4.6 ml. of N hydrochloric acid, warm, and dilute to 25 ml. with distilled water. Measure 2 ml. of this solution into a 15-ml. centrifuge tube.

Prepare standards containing benzidine which are equivalent to 0.001-0.05 mg. of sulfur. These should be prepared so that none is more than twice as concentrated as the next below it. To each add 2 ml. of 0.2 N hydrochloric acid and dilute to 10 ml. Dilute the unknown, containing 2 ml. of 0.2 N hydrochloric acid, to 10 ml.; and add to each of the standards and to the unknown 1 ml. of freshly diluted hydrogen peroxide solution. Mix well and then to each add 0.5 ml. of the 2.5 per cent ferric chloride solution, and again mix. Allow to stand for 10 minutes and read the color within the next 30 minutes. The weight is calculated from the following equation:

$$\frac{R}{U} \times \text{sulfur equivalent of standard} = S \text{ (as } SO_4\text{) in 1 ml. of serum}$$

where R = reading of the standard, and U = reading of the unknown.

If the dissolved precipitate was diluted to 25 ml., multiply the result by 12.5. Wakefield[164] has used a modification of the Hubbard method for the colorimetric determination of sulfate in urine, blood serum and biological fluids.

In the presence of dilute hydrochloric acid, alcohol, and a definite quantity of furfural, a yellow color is obtained with benzidine. Yamazaki[165] has used this reaction to determine the benzidine content of the benzidine sulfate precipitate; or, after such a precipitate has been formed with a measured excess of standard benzidine, the excess of benzidine may be determined in a centrifuged solution.

Procedure. Place 5 ml. of solution to be analyzed in a test tube, and add 2 drops of 0.04 per cent bromophenol blue, and then add sufficient N hydrochloric acid to form a pure yellow color. Add 5 ml. of water and 2 ml. of 0.025 N benzidine hydrochloride solution and 5 ml. of 90 per cent acetone. Allow to stand for a short time and filter. Wash the precipitate three times with small portions of 90 per cent acetone. Dissolve the precipitate in 15 ml. of 0.02 N sodium hydroxide in 50 per cent alcohol, and to this solution add 10 drops of 10 per cent barium chloride solution. Make acid to phenolphthalein and add 10-15 drops of N hydrochloric acid in excess. Dilute to exactly 15 ml., mix, and use 5 ml. of this solution for a colorimetric comparison. Add 2 ml. of 1 per cent aqueous furfural solution, and compare the resulting color with that of solutions containing known quantities of benzidine and treated similarly. Fairly good results are obtained by this method in the analysis of urine.

Benzidine reacts with sodium β-naphthoquinone-4-sulfonate (Folin's amino acid reagent) to form an intense and stable color. Letonoff and Reinhold [133] have developed a procedure for determining sulfate in serum and urine which utilizes this reaction of benzidine sulfate with Folin's reagent in the presence of a sodium hydroxide-sodium borate buffer. Acetone is added after the development of the color to diminish the color of benzidine. The chromogenic power of this reaction is far greater than that with ferric chloride and hydrogen peroxide. Phosphates are removed with uranyl acetate to avoid any error in the precipitation of the sulfate. Results obtained by this method agree very closely with those using Folin's gravimetric method.

Yoshimatsu [128] has also determined sulfate colorimetrically, after precipitating with benzidine, by means of the brown color which is formed when the precipitate is dissolved in an aqueous solution of iodine and potassium iodide and ammonium hydroxide.

Various colorimetric methods which have been used for determining sulfate with the aid of benzidine have been reviewed in a paper by Grant.[166]

Determination of potassium, sodium, calcium and magnesium (total base). Fiske [167] has used benzidine for the indirect determination of sodium potassium, calcium and magnesium (total base) in biological fluids. The method consists in converting these metals to the sulfates, and determining the sulfate by means of benzidine hydrochloride. Stadie and Ross [168] have used a method similar to that of Fiske, but unlike the latter, in which the precipitate of benzidine sulfate is titrated directly with a standard base, the metallic sulfates are determined by titrating the excess benzidine used in an aliquot part of the filtrate after filtering off the benzidine sulfate.

This procedure is based upon the following reactions:

$$B_2SO_4 + Bzd \cdot 2HCl \rightarrow 2BCl + Bzd \cdot H_2SO_4$$

$$Bzd \cdot 2HCl + 2NaOH \rightarrow Bzd + 2NaCl + 2H_2O$$

where B = base and Bzd = benzidine.

After the removal of calcium, magnesium and phosphates, sodium and potassium are determined in biological fluids by the method of Stadie and Ross.[168,169,228]

Reagent. Add 4 g. of benzidine and 45 ml. of N hydrochloric acid to water and dilute with water to 250 ml. Filter and standardize 2 ml. of the reagent by titration with 0.02 N sodium hydroxide.

Procedure. Place an aliquot of a solution containing 0.15 milliequivalent of sodium and potassium, and free of calcium, magnesium and phosphates, in a 50-ml. silica crucible, and add 10-15 drops of sulfuric acid and 2 ml. of concentrated nitric acid. Evaporate to dryness. It may be necessary to add more nitric acid before evaporation is complete. Heat the ash, gently at first, and finally at red heat for 10 minutes. Then cool, dissolve in water, transfer to a graduated cylinder, and dilute to 15.00 ml. with water. Add 2.00 ml. of the benzidine reagent and allow the mixture to stand for 3 minutes. Filter through a No. 40 Whatman 5.5 cm. filter paper, and titrate 15.00 ml. of the filtrate with 0.02 N sodium hydroxide solution, using phenol red as the indicator. The number of milliequivalents of sodium and potassium in the aliquot used in this determination is found from the following equation:

$$\text{Milliequivalents of Na and K} = 0.02 \times (\text{titer of 2.00 ml. benzidine hydrochloride} - \frac{17}{15}\,\text{titer of 15.00 ml. of the filtrate}).$$

Determination of barium. Barium is determined indirectly by a procedure based on the following steps: Precipitate barium with a measured volume of standard sulfuric acid, and determine tne excess sulfuric acid by precipitating with benzidine, and titrating the benzidine sulfate with a standard sodium hydroxide solution. This procedure has been employed by King.[170]

Procedure. Place 2-3 ml. of a solution containing 0.5-2.0 mg. of barium in a conical centrifuge tube and immerse in a beaker of boiling water until hot. Add exactly 4 ml. of standard 0.01 N sulfuric acid and mix well. Cool, and add 2 ml. of a solution containing 4 g. of benzidine and 50 ml. of N hydrochloric acid in 250 ml. Now blow in 3 ml. of 95 per cent acetone from a fine tipped pipet so as to stir the contents of the tube. Allow the mixture to stand for 10 minutes, wash down the walls of the tube with a little acetone, and centrifuge for 5 minutes. Siphon off the supernatant liquid with a fine capillary tube, and again wash by blowing in 3 ml. of 95 per cent acetone to stir the precipitate. Use 1 ml. of acetone to wash down the sides of the tube and again centrifuge for 5 minutes. Carefully pour off the supernatant liquid and invert the tube on a piece of clean filter paper and allow to drain for 2 minutes. Again wash and drain, and blow in 3 ml. of water to stir the precipitate. Place the tube and contents in a beaker of hot water, add a drop of phenolphthalein, and titrate hot with 0.01 N sodium hydroxide solution to a permanent faint pink color. The quantity of barium present may be calculated as follows:

$$4.00 - (\text{ml. of } 0.01 \text{ NaOH used}) = \text{ml. of } 0.01 \text{ N } H_2SO_4 \text{ required to precipitate barium.}$$

$$1 \text{ ml. } 0.01 \text{ N } H_2SO_4 = 0.687 \text{ mg. Ba.}$$

or

$$(4.00 - \text{ml. } 0.01 \text{ N NaOH}) \times 0.687 = \text{mg. Ba.}$$

Determination of tungsten. Gravimetric determination of tungsten. A white flocculent precipitate of benzidine tungstate is formed when benzidine hydrochloride is added to a neutral solution of sodium tungstate. The precipitate is insoluble in water containing an excess of the benzidine hydrochloride. When benzidine tungstate is formed in a cold solution it is difficult to filter and on washing with pure water tends to pass through the filter. If the precipitate is formed from a boiling solution, however, it is obtained in a more compact condition, and on cooling is easily filtered and washed with an aqueous solution of benzidine hydrochloride without loss. The moist precipitate yields a residue of WO_3 when heated to a temperature of 800° C.

Benzidine tungstate is appreciably soluble in hot water containing benzidine hydrochloride, and if the precipitation is carried out in a hot soluton, it is essential to delay the filtration until the mixture is cold. Precipitation may be carried out satisfactorily from a cold solution, if a little dilute sulfuric acid or alkali sulfate is added before treating with benzidine hydrochloride. Under these circumstances, a mixture of crystalline benzidine sulfate and amorphous benzidine tungstate is formed, and this is easily filtered after standing only 5 minutes. The benzidine sulfate is volatile, and is removed during the ignition of the residue to WO_3 Either method gives excellent results if only a small quantity of phosphoric acid is present.[12,13,171-174] The following procedure for the determination of tungsten as tungstate is recommended by von Knorre.[171-173]

Reagent. Triturate 20 g. of benzidine in a mortar with a little water, and transfer the mass to a beaker with about 400 ml. of water. Add 25 ml. of hydrochloric acid (d = 1.2) and heat until solution is complete. Filter and dilute to 1 liter. Use 5.6 ml. of this solution to precipitate 0.1 g. of WO_3.

If the precipitation of benzidine tungstate is carried out in the presence of sulfuric acid, add at least 1 ml. of the reagent for each 10 ml. of 0.1 N sulfuric acid that is added.

Wash liquid. Dilute 10 ml. of the above solution with water to a volume of 300 ml.

Procedure. Convert tungsten to the tungstate by fusion of the material to be analyzed with sodium carbonate. Dissolve the melt in water, add a few drops of methyl orange to the clear solution, and add hydrochloric acid to the appearance of a pink color, and then add 10 ml. of 0.1 N sulfuric acid. Add the benzidine hydrochloride reagent in about 20-40 per cent excess and allow the mixture to stand 5 minutes. Filter, and wash with the dilute benzidine hydrochloride solution until the evaporation of a few drops of the filtrate on a piece of platinum foil leaves no weighable residue. Ignite the moist precipitate at 800° C. and weigh as WO_3.

The following procedure may be used for an approximate separation of tungsten and phosphoric acids:[171]

Procedure. Make the solution containing phosphoric and tungstic acids just acid to methyl orange, and add 3 ml. of hydrochloric acid ($d = 1.12$), and then dilute to 300-400 ml. Heat the mixture to boiling and precipitate with benzidine hydrochloride reagent. Filter, wash the precipitate once or twice with dilute benzidine hydrochloride solution, and boil the precipitate with about 200 ml. of water to dissolve some of the benzidine phosphate. Allow to cool and filter. Wash the precipitate thoroughly with benzidine hydrochloride solution, ignite, and weigh at WO_3.

The residue usually contains a small amount of P_2O_5, which colors the residue a blue-green.

The above method for determining tungsten may also be used in the presence of arsenates. A solution containing both arsenate and tungstate is made slightly acid with hydrochloric acid and treated with a solution of benzidine hydrochloride. The precipitate is ignited and fused with sodium carbonate, and the sodium tungstate is again precipitated with benzidine hydrochloride and ignited to WO_3.[175]

Hinrichsen [176] has used the Knorre method for determining tungsten in steel. If steel contains chromium, a fusion with sodium peroxide is essential, and the solution containing the tungstate and the chromate is precipitated with mercurous nitrate.

Tungsten may be determined in ferrotungsten and special steels by means of a method proposed by Dotreppe.[177] This consists in pouring the tungstate solution into a hydrochloric acid solution of stannous chloride; and, after flocculation of the precipitate, adding a 10 per cent solution of benzidine hydrochloride to precipitate tungsten. The precipitate is washed, ignited, and weighed as WO_3.

Procedure. Pour 50 ml. of the solution to be analyzed, which contains 0.1-0.25 g. WO_3 and 2 g. of potassium chloride, into a cold solution of 4 g. of stannous chloride, $SnCl_2 \cdot 2H_2O$, in 50 ml. of 8 N hydrochloric acid. The acidity of the mixture corresponds to approximately 4 N hydrochloric acid. Shake for a few minutes and add 10 ml. of a 10 per cent aqueous solution of benzidine hydrochloride. Place on a water-bath for 1 hour, and wash the blue precipitate free of tin by decantation with hot N hydrochloric acid which contains 5 g. of benzidine hydrochloride in 1 liter. This point is determined when a little of the wash solution diluted 5-fold with water remains clear and colorless after 5 minutes when treated with hydrogen sulfide. Ignite the filter and precipitate strongly for about 10 minutes and weigh as WO_3.

Titrimetric determination of tungsten. When a solution of benzidine hydrochloride is added to a neutral alkali tungstate, and the precipitation of benzidine tungstate is completed, there is a pronounced hydrolytic adsorption of any excess reagent. This causes a diminution of the pH of the solution. Under these conditions, a single drop of the reagent is sufficient to change the color of methyl red indicator, whereas after the completion of this reaction a much larger quantity of the reagent is necessary. del Campo and Sierra [178] have based a titrimetric method upon this behavior during the precipitation of benzidine tungstate.

A nearly saturated solution of benzidine acetate is added to a neutral alkali orthotungstate solution containing 0.5-1.0 per cent WO_3 and a little methyl red. The color changes sharply at the end-point, owing to hydrolysis of the excess reagent adsorbed on the precipitate. In the absence of a precipitate, a considerable quantity of benzidine is needed to produce a color change. The reagent is standardized against sodium tungstate.

Tungsten in steel is determined by dissolving the sample in hydrochloric or sulfuric acid in the absence of air, and fusing the residue with 4 times its weight of sodium carbonate. The melt is then dissolved in water and titrated with standardized benzidine solution.

Kanchev [179,180] has used a titrimetric method for the determination of tungsten, which is similar in principle to that developed by Raschig [81,82] for the determination of sulfate. This is based upon the precipitation of benzidine tungstate, and the titration with a standard base solution of the tungstic acid which is formed by the hydrolysis of the benzidine salt.

Procedure. Precipitate benzidine tungstate from a warm solution by the addition of an excess of a benzidine hydrochloride solution, and collect the precipitate on a filter. Wash with a little water and transfer the precipitate, together with the filter, to an Erlenmeyer flask and add a little water. Warm to 60° C., and titrate with 0.1 N sodium hydroxide solution, using phenolphthalein as an indicator. The temperature of the mixture is increased to 100° C. at the end of the titration.

In warm solutions of paratungstates and salts of trivalent chromium, the paratungstic acid is not completely precipitated by the addition of mineral acids, due to the formation of complex tungsten-chromium acids.

Kanchev [179,180] claims that results obtained by the above method are exact to within 0.1 per cent, but Mokeev [181] claims that the method gives results which vary with the tungsten content of the samples to be analyzed. He further claims that totally unsatisfactory results are obtained with samples containing less than 0.2-0.3 g. of tungsten.

Determination of selenic acid. Selenates like sulfates are precipitated as the insoluble benzidine salt upon treating a solution of selenic acid or a selenate with benzidine or benzidine salts. Dox [182] first studied this reaction and reported that only about 94 per cent of the selenate is precipitated by this reaction. The reaction is of interest, however, since in the presence of dilute hydrochloric acid, tellurates are not precipitated. Del Campo and Sierra [188] and Kretov [184] have studied this procedure and report that satisfactory results may be obtained with careful attention to detail.

Reagent. Mix 9 g. of pure benzidine in a 200-ml. beaker with 20 ml. of distilled water, and add 20 ml. of glacial acetic acid. Heat until solution is complete. Heat 1.5 liters of water with 75 ml. of 0.1 N hydrochloric acid, and add the benzidine solution in small portions. Cool and allow to stand for 24 hours and filter. Do not use the solution after it has been prepared for more than 3 or 4 days.

Procedure. Add 10 ml. of glacial acetic acid to 800 ml. of the above reagent and dilute with water to 1 liter. To this add slowly and with stirring the selenic acid solution to be determined. Filter, wash the precipitate with 200 ml. of distilled water, boil to remove carbon dioxide, and titrate hot with a standard solution of sodium hydroxide, using phenolphthalein as the indicator.

The solubility of benzidine selenate is somewhat greater than that of the corresponding sulfate, but the loss in accuracy is compensated by the fact that selenites, tellurates and tellurites do not form insoluble salts with benzidine in an aqueous solution.

Detection and determination of fluorides. Feigl and Krumholz [90,91] and Leitmeier and Feigl [185] have used benzidine for the indirect determination of fluorides. A little of the substances to be analyzed is warmed with sulfuric acid and quartz sand, and the silicon tetrafluoride which is evolved is collected in a drop of water. This solution, which contains silicic acid, is then tested by the procedure described on page 296. In this way 0.001 mg. of fluoride can be detected. Nitrates and halogens interfere.

Pertusi [186] and Miller [187] describe a method whereby fluoride is detected by means of the precipitate which forms when a reagent containing benzidine and mercury succinimide is added to a solution containing a soluble fluoride.

Reagent. Dissolve 1.84 g. of benzidine in a little glacial acetic acid and dilute with distilled water to 500 ml. Mix this solution with an equal volume of 0.02 N mercury succinimide solution.

Procedure. Neutralize the solution to be tested with sodium hydroxide, and then make barely acid with acetic acid. Heat to 50° C., and add an excess of the reagent. As little as 0.04 mg. of fluoride in 10 ml. of solution gives a precipitate of $Bzd_2(HF)_4HgF_2$. Oxidizing agents, sulfuric acid and phosphoric acid must be absent.

According to Miller,[187] precipitation is quantitative and fluorine can be determined by precipitating as described above, washing the precipitate with cold water, drying over sulfuric acid and weighing.

Detection of hydrocyanic acid. The reaction of copper salts with benzidine in the presence of cyanides or halides to form benzidine blue has already been discussed in the section on the detection of copper. This reaction takes place due to the increase in the oxidation potential which results when cupric salts are converted to cuprous salts in the presence of cyanides, and the reaction may therefore be applied as a test either for copper or for cyanides. By passing hydrocyanic acid into a solution of copper and benzidine acetates, or by allowing the gas to come in contact with filter paper impregnated with a solution of these reagents, a blue color appears immediately.[188-191,232,243]

Reagent. The solutions of copper acetate and benzidine acetate are prepared and stored separately in dark bottles and the final reagent is freshly prepared as needed.

Solution (*a*). Dissolve 2.86 g. of copper acetate in sufficient water to make 1 liter of solution.

Solution (*b*). Mix 475 ml. of a saturated solution of benzidine acetate with 525 ml. of water.

When ready to use mix solutions (a) and (b) in equal proportions.

Procedure. Place a drop of the solution to be tested in a microcrucible and add a drop of dilute sulfuric acid. Cover the crucible with a strip of filter paper that has been moistened with a drop of the reagent. A blue spot or circle forms on the white paper if the unknown solution contained a soluble cyanide. By this method as little as 0.25γ of cyanogen can be detected.

According to Pertusi and Gastaldi,[188] this reaction is not characteristic for hydrogen cyanide since several substances yield a similar color. In the presence of disodium hydrogen phosphate, however, and in the proper concentration, the reaction can be made specific for hydrogen cyanide.

Reagent. Mix 1 drop of 3 per cent cupric acetate solution with 5 drops of a saturated solution of benzidine acetate and 1 ml. of 10 per cent disodium hydrogen phosphate.

Procedure. Pour the solution to be tested into the above reagent. A blue precipitate forms with as little as 0.027 mg. of hydrogen cyanide in 1 ml. of solution.

Monosodium or trisodium phosphate may be substituted for disodium phosphate in the above procedure. If the solution to be tested contains considerable thiocyanic acid, a blue color may be obtained. To eliminate this possibility of error and to make the test more generally applicable, hydrogen cyanide is removed from the solution in which it is contained by means of a current of carbon dioxide, and led into a reagent prepared by mixing 1 drop of 3 per cent cupric acetate with 5 drops of a saturated solution of benzidine acetate and 0.5 ml. of water.

Determination of cyanide. Hydrogen cyanide may be approximately determined by means of the blue color which is formed when paper impregnated with a cupric acetate-benzidine reagent is exposed to hydrogen cyanide gas.[189,192] The following procedure for determining hydrogen cyanide in air has been used by Deckert.[189]

Procedure. Pass 25 ml. of the air to be analyzed through a filter disc wetted with a benzidine cupric-acetate solution, and compare the resulting color with a color scale obtained by using gases of known hydrogen cyanide content. As little as 0.002 mg. of hydrogen cyanide can be detected by this method and 4-600 mg. determined with an accuracy of ±25 per cent.

The determination of traces of hydrogen cyanide in gases by means of benzidine and cupric acetate is independent within wide limits of the copper and benzidine salt concentration of the test solution. Slight variations in weighing and mixing, as well as in the acetic acid content of the acetate are unimportant. Almost any kind of white filter paper is satisfactory, and other conditions of the test, such as temperature, have little influence on the accuracy of the determination. It is important, however, that the color shade obtained in the test be determined immediately after the formation of the colored compound. Chlorine, bromine, hydrogen chloride, sulfur dioxide and hydrogen sulfide interfere.[193]

In a neutral or acid solution, cyanides and thiocyanates are converted by bromine and water into cyanogen bromide.[254,255]

$$HCN + Br_2 \rightarrow CNBr + HBr$$

$$KSCN + 4Br_2 + 4H_2O \rightarrow KBr + CNBr + H_2SO_4 + 6HBr$$

After removing the excess bromine with sodium arsenite, cyanogen bromide reacts with a solution of benzidine in dilute pyridine to give a deep orange or red color which may be used for the colorimetric determination of cyanide or thiocyanate. Hydrogen cyanide and hydrothiocyanic acid may be differentiated by the fact that the former is volatile on heating the slightly acid solution. The following method is applicable to the determination of cyanide in biological materials.

Reagents. *Pyridine solution:* Add 2 ml. of concentrated hydrochloric acid to 25 ml. of pure redistilled pyridine and dilute with water to 100 ml.

Benzidine hydrochloride solution: Dissolve 2 g. of benzidine hydrochloride in 100 ml. of water.

Procedure. Make 1 ml. of solution, containing up to 3γ of HCN or 6γ of HSCN, acid with acetic acid. Add 0.5 ml. of saturated bromine water and 0.5 ml. of a 1.5 per cent aqueous solution of sodium arsenite. Stopper and allow the mixture to stand 2 hours. Add 1 ml. of this solution to a mixture of 5 ml. of the pyridine reagent and 0.2 ml. of the benzidine hydrochloride solution. Allow to stand for 10 minutes at room temperature for the color to develop. Read the color on a Spekker Absorptiometer in 1-cm. cells, using Ilford micro 2.303 blue filter. Compare with a calibration curve prepared by treating solutions of known cyanide content identically.

Ferricyanide, cyanate, sodium and potassium phosphates, ammonium and sodium chlorides, potassium oxalate, sodium borate and small quantities of cobalt acetate do not interfere.

Detection of thiocyanate. The deep blue precipitate which is formed by the addition of a few drops of a solution of thiocyanate and a few drops of an alcoholic benzidine solution to a solution of copper salts [36,38-40,44,225] may be used for the detection of thiocyanates.

Soluble thiocyanates may also be converted into cyanides under suitable conditions, and the cyanide then identified by the reaction for hydrocyanic acid. Thiocyanates are converted immediately to cyanides upon the addition of potassium permanganate to an acid solution of the thiocyanate. This reaction takes place according to the following equation: [217]

$$5CNS^- + 6MnO_4^- + 8H^+ \rightarrow 6Mn^{+2} + 5SO_4^{-2} + 5CN^- + 4H_2O$$

The test is carried out by adding 1-3 drops of a solution of potassium permanganate that has been acidified with sulfuric acid to a drop of the solution to be tested, and then testing the fumes obtained by warming the mixture with the benzidine-copper acetate paper as described above. It is essential, of course, in testing for thiocyanate by this method that cyanides be absent. If present, the hydrocyanic acid must be completely volatilized by heating the sample with a dilute acid *under a hood.* Chlorides, bromides and iodides must not be present, since they are converted into the corresponding free halogens by potassium permanganate, and these oxidize benzidine to benzidine blue. Any other oxidizing or reducing gases may affect the test.

Determination of thiocyanate. Thiocyanate reacts with bromine and water to form cyanogen bromide. After removing the excess bromine with sodium arsenite, cyanogen bromide reacts with a solution of benzidine in dilute pyridine to give a deep orange or red color. This reaction is suitable for the colorimetric determination of thiocyanate. For the details of this procedure, see section of determination of cyanide.

Detection of cyanates. A red color changing to brown is formed when 2-5 drops of 6 per cent alcoholic benzidine solution and a few drops of cupric acetate solution are added to a neutral or weakly acid solution of a cyanate. This reaction has been used by Fearon [218] as a test for cyanates.

Detection of ferrocyanides and ferricyanides. The usual test for ferricyanides, which is based upon the formation of Turnbull's blue with ferrous salts, is not for several reasons suitable for a spot test. The ferricyanide is often reduced by the cellulose of the paper on which the test is carried out to give a blue color with ferric salts which are used for detection of ferrocyanides. If the test is carried out on a spot plate, confusion is also likely to result from the fact that ferricyanides not infrequently contain ferrocyanides, which react with ferric salts usually present in the ferrous salts. Further, white ferrous ferrocyanide, which may first form, turns blue on exposure to air. For these reasons, and because of the additional fact that it is difficult to effect a separation of ferri- and ferrocyanides, a more satisfactory test for ferricyanides in the presence of ferrocyanides is based upon the oxidation of benzidine acetate by soluble ferricyanides.

Benzidine acetate is oxidized by ferricyanides to form the insoluble blue meriquinoid oxidation product. This reaction may be used in the presence of ferrocyanides with which benzidine forms a white salt of ferrocyanic acid similar to that of benzidine sulfate. In the presence of ferrocyanides, however, greater quantities of benzidine are required for the detection of ferricyanides. The following method is used for the detection of ferricyanides.[191,194,195]

Reagent. Saturate a 2 N solution of acetic acid in the cold with benzidine.

Procedure. Place a drop of the solution to be tested on a spot plate and add 1 drop of benzidine acetate reagent. If ferricyanides are present, a blue precipitate or color appears. As little as 1γ of potassium ferricyanide at a concentration limit of 1:50,000 can be detected by this method.

Small amounts of ferricyanides are detected in the presence of large quantities of ferrocyanide by first adding sufficient lead acetate to precipitate insoluble lead ferrocyanide. Ferricyanides remain in solution, and on the addition of benzidine, the white precipitate becomes blue in color. By means of this treatment as little as 5γ of potassium ferricyanide can be detected in the presence of 1,000 times as much ferrocyanide.

Determination of ferricyanide and ferrocyanide. A white precipitate of $3\ \mathrm{Bzd \cdot H_4Fe(CN)_6 \cdot H_2O}$ is formed when benzidine hydrochloride is added to a solution of a ferrocyanide. The solubility of this compound is about 8 mg. per 100 ml. of water. Cumming[196,197] has used this reaction as the basis for a method for determining ferrocyanide. For the gravimetric determination, approximately 0.2 g. of a soluble ferrocyanide is treated with a slight excess of benzidine hydrochloride solution, and the resulting precipitate is filtered, washed, dried and ignited to Fe_2O_3. The factors for calculating ferrocyanide as the potassium, sodium and calcium salts are, respectively, 4.599, 3.799, 3.649.

A titrimetric method is also based upon this reaction. A measured excess of standard benzidine hydrochloride solution is added to a neutral solution of a ferrocyanide, and the free hydrochloric acid in the filtrate is estimated with a standard alkali with phenolphthalein as the indicator. This procedure is based upon the following reaction:

$$3[\mathrm{Bzd \cdot 2HCl}] + \mathrm{M_4Fe(CN)_6} \rightarrow \mathrm{3Bzd \cdot H_4Fe(CN)_6} + \mathrm{4MCl} + \mathrm{2HCl}$$

The hydrochloric acid formed is equivalent to one-third that present in the benzidine hydrochloride used in the reaction: hence, if 1 ml. of the alkali solution is equivalent to b ml. of benzidine hydrochloride, and n and x are the number of ml. benzidine hydrochloride added and used in the reaction respectively, then the number of ml. of alkali required after the reaction is

$$a = \frac{(n-x)}{b} + \frac{x}{3b}$$

hence $x = 1.5\ (n - ab)$.

Since the concentration of the benzidine hydrochloride is known, the amount of the original ferrocyanide can be calculated. The value of $\frac{x}{3b}$ is equal to the volume of standard alkali used, and this is identical to free hydrochloric acid produced in the reaction, and is proportional to the amount of ferrocyanide present.

According to Cumming and Good,[197] ferricyanide may be determined in a manner similar to that employed for ferrocyanide, but a considerable excess of benzidine hydrochloride is required for complete precipitation. A gravimetric or titrimetric procedure may be used. The titrimetric procedure is based upon the reaction:

$$3[\mathrm{Bzd\cdot 2HCl}] + \mathrm{M_3Fe(CN)_6} \rightarrow \mathrm{3Bzd\cdot H_3Fe(CN)_6} + \mathrm{3MCl} + \mathrm{3HCl}$$

From this equation it may be seen that the hydrochloric acid formed is equal to one-half the quantity present in the benzidine hydrochloride. Using the same discussion as applied to the calculation of the results of the procedure for ferrocyanides, it may be seen that for ferricyanides, $x = 2(n - ab)$.

Detection of nitrites. Nitrites may be detected by means of the yellow to red color which forms when benzidine or a benzidine salt is added to an acidified solution of nitrite.[198-203,230] This reaction may also be modified by adding substances which are capable of coupling with the diazotized benzidine to form highly colored products.[204-206]

A solution of 1-2 g. of benzidine in 100 ml. of 50 per cent acetic acid and diluted with 300 ml. of water gives no reaction with nitrates or chlorates, but yields an intense yellow color with nitrites. As little as 0.05 mg. of N_2O_3 per liter gives this test, but 100-200 ml. of an aqueous solution of the nitrite and 10 ml. of the reagent must be used at this dilution.[198] Ronzhina [200] has used this reaction as the basis for a spot test for nitrites.

Procedure. Place a drop of the solution to be tested on a strip of filter paper and add a drop of a solution of benzidine in acetic acid. A deep red to yellowish-pink color forms, depending upon the concentration of the nitrite. This test is very sensitive.

If the reagent and solution to be analyzed contain about the same amount of acetic acid, the only anion which interferes with this test is chromate, which gives a deep blue color. If chromate is present, the test is modified as follows:

Procedure. Place a drop of a concentrated solution of barium chloride on a strip of filter paper, and place a drop of the solution to be tested in the center of the wet spot. The chromate is thus fixed as insoluble barium chromate, while the nitrite diffuses to the outer edge of the ring. When the still moist spot is treated with a little benzidine solution, the center containing barium chromate is colored blue, while the outside circle appears red to yellow if nitrites are present.

If the solution to be tested is strongly acid it must first be neutralized by an alkali before applying the benzidine test. It is not necessary to remove the cations of the heavy metals.

Determination of nitrite. Primot[201] has used the reaction of benzidine with acid solutions of nitrites for the colorimetric determination of small quantities of nitrites in water.

Reagent. Prepare a 1-1.5 per cent solution of benzidine in 30-40 per cent alcohol.

Procedure. Add about 5 drops of the above reagent and 5 drops of acetic acid to 10 ml. of water to be analyzed. Estimate the nitrite by comparing the yellow color which forms with that of standard solutions containing known quantities of nitrites which are treated in a similar manner. The color reaches its maximum intensity after about 30 minutes.

Bittencourt and Barreto[206] and Eegriwe[204] have modified the above reaction for nitrite by coupling the diazotized benzidine with β-naphthol. The test is carried out as follows:

Procedure. Place the solution to be analyzed in a test tube and acidify with 2 N sulfuric acid. Then dip a stirring rod in a 1 per cent solution of benzidine hydrochloride and expose the drop which adheres to it to the gases issuing from the mouth of the test tube. Then transfer the drop to a strip of filter paper and add a drop of 0.04 per cent β-naphthol solution, and a drop of a solution of sodium hydroxide or ammonium hydroxide. An intense red coloration appears if nitrites are present. In this manner 0.004 mg. of nitrite can be detected in 5 ml. of solution.

Vagi[205] has recommended a similar test, but has used sodium 1-amino-8-naphthol-3,6-disulfonate as the coupling agent. The reagent is prepared by dissolving 1 g. of benzidine and 1 g. of the sodium aminonaphtholdisulfonate in 100 ml. of 80 per cent acetic acid and diluting the mixture with 300 ml. of water.

Determination of chlorine. A brilliant blue-green color is obtained when benzidine hydrochloride is added to a solution containing free chlorine, and this color has been used as the basis for the colorimetric determination of chlorine.[24,207-209] The color fades rapidly so that artificial standards of copper sulfate and picric acid are needed for the comparison. The reaction is influenced by the presence of carbonates and organic matter and the quantity of reagent added, and to some extent by the pH of the solution. In general the *o*-tolidine method seems preferable to that employing benzidine.

Reagents. *Benzidine solution.* Dissolve 2.3 g. of benzidine in 100 ml. of 5 per cent hydrochloric acid.

Standard solution. This solution is prepared empirically to match the color of a solution containing 0.003 mg. of free chlorine per 100 ml. of solution. Mix a 15 per cent solution of copper sulfate and a 0.5 per cent solution of picric acid until the desired blue-green tint is obtained. Dilute this mixture until the color matches that obtained by treating a freshly prepared solution containing 0.003 mg. of free chlorine per 100 ml. by the following procedure.

Procedure. Dilute a volume of the sample containing 0.001-0.01 mg. of free chlorine to 100 ml. Add 1 drop of the benzidine reagent, and compare immediately with the artificial standard by balancing.

Detection of oxidizing agents. The oxidation of benzidine to the blue meriquinoid oxidation product, and the use of this reaction for the detection of many substances, has already been discussed in several of the preceding sections, but in addition to the oxidizing agents (or substances which are capable of auto-oxidation reactions) which have already been mentioned, a number of other ions may be also detected.

Neutral or weakly acid solutions of alkali persulfates yield a blue color on the addition of benzidine acetate, due to the formation of the oxidation product of benzidine. Alkali peroxides, perborates, and hydrogen peroxide do not react with benzidine under these conditions, and consequently persulfates may be detected in the presence of these other per-compounds.[226]

Procedure. Place a drop of a neutral or a slightly acetic acid solution to be tested on a spot plate, and mix with a drop of a 2 per cent solution of benzidine in dilute acetic acid. A blue coloration appears if persulfates are present. The test is more sensitive in the neutral solution than in an acetic acid solution. In the former case 0.25γ of potassium persulfate can be detected, while in an acid solution the reaction is sensitive to only 1γ of potassium.

Chromates, permanganates, ferricyanides and the hypohalites must be absent, since they, too, oxidize benzidine to benzidine blue. Chlorates, perchlorates, bromates, iodates and nitrates do not react under the conditions of the test, but they reduce the sensitivity of the persulfate reaction.

Monnier[210] has modified the persulfate test by carefully overlaying the surface of the persulfate solution with a solution of benzidine. A dense blue precipitate forms at the zone of contact of the two liquids. Benzidine has been used to detect persulfates in flour.[12,211]

Periodates give a reddish-brown color with benzidine, and in the absence of interfering substances this reaction may be used for the detection of periodates. Perchlorates, chlorates, iodates, nitrates, perborates and percarbonates give no color and no precipitate with benzidine.

Chlorates, nitrates and iodates may be detected with the aid of benzidine by means of the following procedure:[212,213]

Procedure. Mix a little of the solution to be tested and a little benzidine sulfate in a test tube, and then allow 3-4 ml. of concentrated sulfuric acid to run down inside of the tube. An orange color forms with nitrates, chlorates or iodates at the junction of the two liquids.

Pozzi-Escot[247] has found that with nitrate, benzidine hydrochloride forms a white crystalline compound which is suitable for the microchemical detection of nitrates.

Arnold and Mentzel[214] have used benzidine for the detection of ozone. A reagent paper prepared by impregnating filter paper with a saturated alcoholic solution of benzidine is colored brown by ozone. This paper is colored blue by bromine and nitrites, and a blue and then reddish-brown with chlorine. Avellar de Loureiro[215] has recommended the use of a saturated solution of benzidine in petroleum benzine for the detection of ozone in cod liver oil.

Detection of ammonia. Benzidine may be used for the detection of ammonia in air after first having been diazotized with sodium nitrite and hydrochloric acid. A test paper that has been impregnated with the diazo compound gives a colored compound with ammonia. By means of this reaction it is possible to detect about 0.015 mg. of ammonia in 1 liter of air.[219]

Detection of sulfite. An intense blue color develops when a drop of an acetic acid solution of benzidine is added to a little solid nickelic hydroxide, $Ni(OH)_3$. Since the auto-oxidation of sulfurous acid induces the oxidation of $Ni(OH)_2$ to $Ni(OH)_3$, this reaction may be used for the indirect detection of sulfites.[32] The test is carried out by passing sulfur dioxide and air into a suitable receiver containing freshly precipitated $Ni(OH)_2$ that has been washed free of alkali. The precipitate is filtered and touched with a drop of an acetic acid solution of benzidine. If sulfur dioxide is present in the gas, a blue color appears. This test is sensitive to 0.4γ of SO_2 at a concentration of 1:125,000.

Determination of hydrogen chloride. Vernon and Whitby[220] have used benzidine for the absorption of hydrogen chloride gas.

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BENZYLAMINE

C_7H_9N Mol. Wt. 107.15 Beil. Ref. XII, 1013

$$C_6H_5—CH_2—NH_2$$

Uses: Detection of molybdenum, tungsten and vanadium.

Determination of cerium, lanthanum, neodymium, praseodymium, thorium and zirconium.

Benzylamine is a colorless liquid having a strongly alkaline reaction. Its sp. gr. is 0.983, and it boils at 184° C. It is miscible with water, alcohol and ether.

Preparation: Pass dry ammonia into absolute alcohol until a 15 per cent solution is obtained, and then add such quantity of benzyl chloride that the ratio of ammonia to benzyl chloride is 20:1. Allow the mixture to stand 5 days at room temperature, and then slowly heat on a water-bath in a flask equipped with a reflux condenser. Filter off the ammonium chloride which separates to prevent bumping, and continue heating until all the ammonia is expelled. Mix the residue with 2 or 3 times its volume of water, warm on a water-bath, and acidify with dilute hydrochloric acid. Heat nearly to boiling and add hot water as long as any of the material dissolves. Filter and wash the residue, which consists of tribenzylamine, with hot water. Evaporate the filtrate to one-half its volume and allow to stand. Filter off the white crystals of dibenzylamine and wash with cold water. Evaporate the filtrate nearly to dryness, cool, add concentrated sodium hydroxide, and extract benzylamine with ether. Dry the extract with a large quantity of sodium hydroxide and distill off the ether. The reagent is recovered by distillation. B.P. 180-190° C. Purify by a second distillation.[1]

Detection of molybdenum, tungsten and vanadium. Martini [2] has used benzylamine in a microchemical test for molybdenum, tungsten and vanadium.

Procedure. To 1 drop of a 1 per cent ammonium molybdate solution, add small quantities of pyrocatechol until the liquid is orange-red in color, and then add with the aid of a small stirring rod a tiny drop of benzylamine. Next add a little 15 per cent acetic acid and stir quickly with a glass rod. Round, orange groups of crystals form.

Similar crystalline compounds are obtained with vanadates and tungstates. A light yellow color is obtained with vanadium and a black color with tungsten.

The probable composition of the molybdenum compound is given by the following formula: $[OMo^{V}OH(O—C_6H_4O)_2]N_2·CH_3—COO—C_6H_5CH_2NH_2$.

Determination of metals. Jefferson[3] has studied the use of benzylamine as a precipitant for zirconium, thorium, cerium, lanthanum, neodymium and praseodymium.

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BENZYLIMIDODI (4-METHOXYPHENYL) METHANE

$C_{22}H_{21}O_2N$ Mol. Wt. 331.39

$$(CH_3O—C_6H_4)_2{=}C{=}N—CH_2—C_6H_5$$

Use: Detection of elementary sulfur.

This reagent is a pale yellow crystalline solid melting at 89-91° C. It is soluble in ether and chloroform, but is only slightly soluble in petroleum ether.

Preparation: Place one mole of finely powdered *p,p'*-dimethoxybenzophenone in a flask fitted with a condenser, and add 3 moles of pure thionyl chloride. Heat 5 hours at the boiling point on a water bath, with the exclusion of moisture, and after the reaction is completed, distill off the excess thionyl chloride *in vacuo.* Dissolve the red crystalline mass remaining in the flask (*p,p'*-dimethoxybenzophenone chloride) in a sufficient quantity of absolute ether, and add in small portions 3 moles of benzylamine. Heat the mixture an hour on a water-bath, and separate the liquid from the residue with suction. Wash the residue (benzylamine hydrochloride) several times with absolute ether and combine the filtrates. Pass dry carbon dioxide into the solution to remove any unchanged benzylamine. Filter, and evaporate the filtrate to dryness *in vacuo.* Purify the residue by crystallization from benzine (B.P. 110°).

Detection of free sulfur. When a little of the reagent is heated with free sulfur, a blue compound is formed which can be extracted with benzene. This reaction may be used as a very sensitive test for free sulfur.[1,2]

Procedure. Grind a little of the material to be tested (biological material) with the reagent, and place the mixture in a melting-point tube. Immerse the tube for 5 minutes in a bath previously heated to 210° C. In the presence of free sulfur, the benzene extract of this mixture is colored blue. If a crystal of mercuric chloride is added to the blue solution, the blue color fades slowly, and the surface of the crystal is colored an intense red.

Free sulfur, in amounts as low as 0.04 mg., can be detected by this reaction in the presence or absence of combined sulfur.

The blue color which appears in this reaction is due to the formation of *p,p'*-dianisylthioketone, $CH_3O—C_6H_4—CS—C_6H_4—OCH_3$. The red color with mercuric chloride is caused by the formation of an addition compound of the following composition, $(CH_3O—C_6H_4)_2=C(Cl)—SHgCl$.

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BIGUANIDE SULFATE

Synonym: Guanyl guanidine sulfate

$C_2H_7N_5$ Mol. Wt. 101.08 Beil. Ref. III, 93(44)

$$H_2N—C(=NH)—NH—C(=NH)—NH_2$$

Use: Determination of copper and nickel.

Biguanide sulfate occurs as water-soluble colorless crystals.

Preparation: Mix intimately 1 part of dry dicyandiamide and 2 parts of dry ammonium iodide, and heat on a sand bath. Keep the temperature of the molten mass at 173° C. for 5 minutes. Cool, extract the mass with water, and make alkaline with ammonium hydroxide. Filter, and precipitate copper biguanide sulfate by the addition of an ammoniacal solution of copper sulfate. Filter off the precipitate of the copper salt, wash, and decompose with 10 per cent sulfuric acid. Allow the mixture to cool, and collect the crystals of biguanide sulfate which form. Recrystallize from water at 60° C.[1]

Determination of copper. Copper biguanide sulfate forms as a pink, silky precipitate upon the addition of biguanide sulfate to an ammoniacal solution of copper sulfate. The solubility of this complex copper salt at or below 90° C. is negligible. The precipitate has the composition $[Cu(C_2H_7N_5)_2]SO_4 \cdot 3H_2O$, and may be weighed directly after washing and drying at 50-70° C. Zinc and cadmium do not interfere with the copper determination, and molybdenum and tungsten cause no interference if present as molybdate and tungstate. Metallic ions which are precipitated by ammonium hydroxide, such as iron, aluminum, chromium, bismuth, antimony and mercury; or ions which form insoluble sulfates, such as lead, barium, calcium and strontium, interfere and must be absent. Cobalt and nickel form slightly soluble complex salts similar to that with copper, and consequently are also precipitated with biguanide sulfate. Nitrate, phosphate, arsenate, arsenite and ferrocyanide form sparingly soluble copper biguanide salts, and therefore must also be absent.[2]

Procedure. To a volume of the solution containing 1-30 mg. of copper, and no nitrate, add 0.1-0.2 g. of ammonium sulfate. Carefully add ammonium hydroxide until the solution turns to a deep blue. Dilute to 120 ml., warm, and add dropwise and with constant stirring an excess of biguanide sulfate solution. Cool the mixture with ice to a temperature below 10° C., and allow to stand at that temperature for about half an hour. Filter through a sintered glass crucible, and wash, first with cold water (10° C.) until free of sulfate, then with alcohol, and finally with ether. Dry at 50-60° C. and weigh as $[Cu(C_2H_7N_5)_2]SO_4 \cdot 3H_2O$. The factor for copper is 0.1530.

When an ammoniacal solution of copper sulfate is treated with a solution of biguanide sulfate, the copper ion is converted into the stable inner-complex copper biguanide ion. This complex does not give the characteristic reactions of the simple copper ion. This fact has been utilized for the titrimetric determination of copper. Rubeanic acid is used as an external indicator. The end-point of the reaction is indicated by the disappearance of the reaction of the copper ion. Since each copper atom is associated with two molecules of biguanide, the quantity of copper present may easily be calculated from the amount of biguanide used.

Procedure. Add ammonium hydroxide dropwise to the copper sulfate solution until the color turns blue, and then titrate with standard biguanide sulfate solution with constant stirring. From time to time remove a drop of the mixture with a stirring rod and transfer to a strip of quantitative filter paper. Treat the spot with a drop of an alcoholic solution of rubeanic acid, and dry over a bunsen flame. The end-point is indicated by the disappearance of the black spot on the paper. The determination is made more accurate by making a duplicate titration in which nearly the entire quantity of biguanide sulfate required is added at one time, and the titration finished as described above.

A sharp end-point is not obtained in the presence of cadmium. Anions and cations which interfere with the gravimetric determination also interfere in the above procedure.

Determination of nickel. Biguanide sulfate is used to determine nickel in the presence of aluminum, chromium, iron, zinc, titanium, uranium and beryllium.[3]

Procedure. Make the solution to be analyzed acid, and add sufficient Rochelle salt to prevent the precipitation of other metals. Then add an excess of a faintly ammoniacal 1 per cent solution of biguanide sulfate. Cool, and add an excess of 2 N sodium hydroxide with stirring, and then add a little more. If zinc is present, add sufficient sodium hydroxide to form the zincate. Allow the cold solution to stand until the precipitate has settled, and then filter. Wash free of alkali with a minimum quantity of cold water, and dissolve the precipitate in a measured excess of sulfuric acid. Titrate the excess at room temperature with standard sodium hydroxide solution in the presence of Wesselow's indicator. The reaction is expressed by the following equation:

$$\mathrm{Ni(C_2H_7N_5)_2(OH)_2 + 2H_2SO_4 \rightarrow NiSO_4 + (C_2H_8N_5)_2SO_4 + 2H_2O}$$

$$\mathrm{H_2SO_4} = \frac{\mathrm{Ni}}{2} \text{ or } 1.0 \text{ ml. N } \mathrm{H_2SO_4} = 0.0146725 \text{ g. Ni.}$$

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2. P. Ray and J. Roy-Chowdhury, *J. Indian Chem. Soc.* **18**, 149-54 (1941); *C.A.* **35**, 7871 (1941).
3. A. K. Majundar, *J. Indian Chem. Soc.* **20**, 289-90 (1943); *C.A.* **38**, 2283 (1944).

n-BUTYLAMINE

$C_4H_{11}N$ Mol. Wt. 73.14 Beil. Ref. IV, 156

$CH_3—CH_2—CH_2—CH_2—NH_2$

Use: Detection of hydrocyanic acid, iridium, osmium, palladium and platinum.

n-Butylamine is a colorless liquid possessing an ammoniacal odor. Its sp. gr. is 0.742. It boils at 78° C. and melts at −50° C. It is miscible with water, alcohol, and ether.

Preparation: Dissolve 175 g. of butyraldoxime in 4 liters of absolute alcohol contained in a flask, and heat to boiling on a steam bath. Fit the flask with a reflux condenser having a very wide inner tube. When the alcohol begins to boil, shut off the steam, and keep at the boiling temperature by the introduction of strips of sodium through the top of the condenser. The total amount of sodium used is 500 g., and this should be added as rapidly as possible without loss of alcohol. The last 150 g. may be added rapidly. When the sodium has dissolved, cool the mixture, and dilute with 5 liters of water. Distill into a solution of 300 ml. of concentrated hydrochloric acid in 300 ml. of water. The distillate is delivered below the surface of the hydrochloric acid solution. Distill as long as any basic material distills over. Frothing near the end of the distillation may interfere, and at this point add an additional 3 liters of water. The total distillate is about 8-9 liters. Remove the alcohol, water, and unreacted oxime by distilling at 20-30 mm. Cool the flask and fit with a reflux condenser through which 1 liter of 40 per cent potassium hydroxide is added. Cool and transfer to a separatory funnel. Remove the lower alkaline layer, and add solid potassium hydroxide to the amine in the funnel. Dry 24-30 hours and withdraw the aqueous layer. Add an additional quantity of solid potassium hydroxide until no further separation of alkaline solution occurs. Decant through the top of the funnel into a 250-ml. modified Claisen flask and distill. Butylamine distills at 75-80° C.[1]

Detection of the platinum metals. Whitmore and Schneider [4] have investigated the use of *n*-butylamine hydrochloride as a microchemical reagent for the detection of the platinum metals. Their results are shown in Table 40.

TABLE 40.—DETECTION OF THE PLATINUM METALS WITH *n*-BUTYLAMINE HYDROCHLORIDE

Test Material	Description
$RuCl_3$	Test drop gradually turns green.
$RhCl_3$	No apparent reaction.
$PdCl_2$	A great many, small, reddish-yellow, rectangular plates of considerable size, appear immediately. Appears to be an excellent test for palladium.
Na_2OsCl_6	Many, bright-yellow, hexagonal plates develop gradually. These are all of fair size. Scratching the slide with a glass rod brings down a very abundant crop of these crystals.
$IrCl_4$	A great many purplish-red hexagonal crystals appear.
H_2PtCl_6	A very dense mass of leaf-like structures form immediately.
$AuCl_3$	No apparent reaction.

Microdetection of hydrocyanic acid. When uric acid is oxidized with nitric acid, the alloxan thus formed may be detected by transforming it to oxaluramide by means of the hydrogen cyanide-catalyzed reaction of Deniges.[2] The use of various amines instead of ammonia in the formation of the oxaluramide increases the sensitivity of the reaction. Butylamine gives the most sensitive test.[3]

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2. G. Deniges, *Mikrochemie.* 4, 149-54 (1926); *C.A.* 21, 2628 (1927).
3. A. Martini, *Pub. inst. investigaciones microquim., Univ. nacl. litoral,* 1, 61-4 (1937); *C.A.* 34, 344-5 (1940).
4. W. F. Whitmore and H. Schneider, *Mikrochemie.* 17, 279-319 (1935).

p-CHLOROANILINE

C_6H_6NCl Mol. Wt. 127.57 Beil. Ref. XII, 607

$Cl—C_6H_4—NH_2$

Use: Determination of beryllium.

Separation of titanium from beryllium.

p-Chloroaniline is a crystalline solid which melts at 69-70° C. and sublimes at 70-71° C. It boils at 230-231° C. It is soluble in hot water, alcohol, ether, acetone and carbon disulfide.

Preparation: Dissolve 10-15 g. of acetanilide in 1 liter of water, and introduce a stream of chlorine gas with gentle cooling as long as a white precipitate of 4-chloroacetanilide forms. Filter and heat the 4-chloroacetanilide for 1 hour at 150° C. with sufficient concentrated sulfuric acid to dissolve it. Pour the mixture into water, make alkaline with sodium hydroxide to precipitate most of the *p*-chloroaniline, and extract the filtrate with ether to obtain the remainder of the compound. Dissolve in water, boil the solution with a little animal charcoal, and filter. On evaporating the solution, the reagent crystallizes as cubes or needles.[1,2]

Determination of beryllium and separation of titanium from beryllium. Dixon[3] has used *p*-chloroaniline for the separation of titanium from beryllium as a preliminary to the determination of small quantities of beryllium in rocks.

Procedure. Heat to boiling 250 ml. of a hydrochloric acid solution containing 5-10 mg. of TiO_2 and 5-40 mg. of BeO. Carefully neutralize by the dropwise addition of ammonium hydroxide with stirring until the mixture is turbid but still distinctly acid to litmus. Then add 1-1.5 g. of *p*-chloroaniline. Cover with a watch glass and bring the mixture to boiling, and keep at the boiling point for 3 minutes. Filter, wash the precipitate with hot water until free from chlorides, and ignite and weigh. Under these conditions all titanium is precipitated as $Ti(OH)_4$. No beryllium is precipitated.

The same accuracy is not obtained if precipitation is carried out in sulfuric acid instead of hydrochloric acid solution. The error is insignificant if only small quantities of beryllium are present, but with larger quantities of beryllium the quantity of titanium found is too great.

1. E. E. Slosson, *Am. Chem. J.* 29, 302 (1903).
2. W. J. Jones and K. J. P. Orton, *J. Chem. Soc.* 95, 1058 (1909).
3. B. E. Dixon, *Analyst.* 54, 268-74 (1929); *C.A.* 23, 4636 (1929).

CUMIDINE

Synonym: *p*-Isopropylaniline

$C_9H_{13}N$ Mol. Wt. 135.20 Beil. Ref. XII, 1147

$$(CH_3)_2CH—C_6H_4—NH_2$$

Use: Determination of tungsten.

Cumidine is a liquid boiling at 225° C. It is insoluble in water.

Preparation: Heat together at 230° C. for 8 hours in a tube, a mixture of 1 mole of aniline, 1 mole of isopropyl alcohol and 1 mole of zinc chloride. Separate by fractional distillation the portion boiling at 211-230° C. Form the sulfate with sulfuric acid, and repeatedly crystallize from warm water containing a little sulfuric acid. Add an excess of ammonia to the sulfate to form a nearly colorless oil, which distills between 217-220° C.[1]

Determination of tungsten. Kafka[2] has used cumidine for the gravimetric determination of tungstic acid.

Reagent. Shake 5 g. of cumidine with about 10 ml. of water and 5 ml. of concentrated hydrochloric acid, and then dilute to 100 ml. Prepare a wash liquid by diluting 5 ml. of the reagent with 100 ml. of water.

Procedure. To 50 ml. of sodium tungstate solution, add 15 ml. of the reagent with constant stirring. Allow to stand 1 hour and filter. The supernatant liquid should remain clear. Ash in a platinum crucible, and ignite to constant weight. The factor for WO_3 is 0.6956.

1. E. Louis, *Ber.* 16, 111 (1883).
2. E. Kafka, *Z. anal. Chem.* 52, 601-6 (1913); *C.A.* 7, 3939 (1913).

3,5-DIAMINOBENZOIC ACID

$C_7H_8O_2N_2 \cdot H_2O$ Mol. Wt. 170.17 Beil. Ref. XIV, 453

$$HO_2C—C_6H_3(NH_2)_2$$

Use: Detection and determination of nitrite.

3,5-Diaminobenzoic acid occurs as the crystalline monohydrate. It melts at 228° C. It is slightly soluble in water, but is more readily soluble in alcohol and ether. The aqueous solution decomposes on standing.

Preparation: Dissolve 3,5-dinitrobenzoic acid in an excess of ammonium hydroxide and saturate with hydrogen sulfide. Evaporate until the odor of the sulfide is no longer detectable, and then filter and make the filtrate strongly acid with acetic acid.[1]

Detection and determination of nitrites. In the original Griess reaction for nitrite, which depends upon the diazotization of a primary amine, 3,5-diaminobenzoic acid was the substance first employed. This reagent, however, has since been replaced by various compounds which have proved more suitable.[1,2]

1. P. Griess, *Z. anal. Chem.* **10**, 92 (1871).
2. P. Griess, *Ann. chem. pharm.* **154**, 333.

4,4′-DIAMINO-1,1′-DIANTHRAQUINOYL AMINE

$C_{28}H_{17}O_4N_3$ Mol. Wt. 459.42

$$C_6H_4{=}(CO)_2{=}C_6H_2(NH_2){-}NH{-}(NH_2)C_6H_2{=}(CO)_2{=}C_6H_4$$

Use: Determination of boron.

Preparation: The amine is prepared by the reduction of 4,4′-dinitro-1,1′-dinathraquinoyl amine [1] with sodium sulfide. To purify the crude product, dissolve in 10 times its weight of 98 per cent sulfuric acid and filter. Dilute the filtrate with water until the acid content is 83 per cent. Filter off the precipitate, and wash, first with 83 per cent sulfuric acid, and then with water.

Determination of boron. 4,4′-Diamino-1,1′-dianthraquinoyl amine dissolves in sulfuric acid to form a blue solution, which changes to an indefinite orange color when heated to 150° C. In the presence of boric acid, the change at 150° C. is to a dull greenish-olive color. This reaction has been used by Beckett and Webster [2] for the determination of boron in organic materials.

Reagent. Dissolve 0.1 g. of the amine in 100 ml. of 98 per cent sulfuric acid.

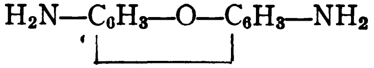
Procedure. Mix 0.25 g. of a sample containing not more than 0.5 per cent boric acid with 0.3 g. of sodium carbonate, and fuse in a platinum dish until the residue is white. Dissolve in a little 97-98 per cent sulfuric acid, and dilute to 50 ml. with the same acid. Transfer 2-, 5-, and 9-ml. portions of this solution to suitable vessels, and to each add 1 ml. of the reagent solution. Dilute each sample to 10 ml. with 98 per cent sulfuric acid. Heat for 30 minutes at 150° C. in a glycerol bath, and measure the optical density of the green-olive solution at 6200 Å in a 1-cm. cell of a Hilger visual spectrophotometer. Deduct from the result the value obtained with a blank containing only sodium carbonate and sulfuric acid. A density difference of $1.0 \equiv 0.00467$ mg. of boric acid per ml.

1. A. Eckert and K. Steiner, *Monatsh.* **35**, 1129 (1914).
2. E. G. Beckett and M. F. H. Webster, *Analyst* **68**, 306 (1943); *C.A.* **38**, 38 (1944).

2,7-DIAMINODIBENZOFURAN

Synonym: 2,7-Diaminodiphenyleneoxide

$C_{12}H_{10}ON_2$ Mol. Wt. 198.20



$H_2N—C_6H_3—O—C_6H_3—NH_2$

Uses: Detection of cobalt.

Determination of copper.

2,7-Diaminodibenzofuran is obtained as needles by crystallizing from water. It melts at 150-152° C. The hydrochloride is insoluble in water.

Preparation: 2,7-Diaminodibenzofuran is prepared by heating 2,2′-benzidinedisulfonic acid with 40 per cent sodium hydroxide solution for 6-8 hours under 36 atmospheres pressure.

Detection of cobalt. Brau[1] has used 2,7-diaminodibenzofuran in place of benzidine in testing for cobalt by the method of Chiarottino.[2] In this method a mixture of benzidine and dimethylglyoxime gives an orange-red color when added to a solution containing a cobalt salt. For details, see section on dimethylglyoxime.

Determination of copper. Brau[3] has also substituted 2,7-diaminodibenzofuran for benzidine in the Fleming-Spacu reaction for copper. In the presence of cyanide, cyanate or thiocyanate, 2,7-diaminodibenzofuran reacts with solutions of copper salts to yield blue or violet needles. The sensitivity of this reaction makes 2,7-diaminodibenzofuran a suitable reagent for determining copper.

1. E. F. Brau, *Rev. facultad cienc. quim.* (*Univ. La Plata*). **8**, Pt. 2, 65-70 (1933); *C.A.* **28**, 2641 (1934).
2. A. Chiarottino, *Industria chimica.* **8**, 32-3 (1933); *C.A.* **27**, 2396 (1933).
3. E. F. Brau, *Rev. facultad cienc. quim.* **10**, 43-5 (1935); *C.A.* **30**, 7059 (1936).

p-DIAMINODIPHENYLAMINE

$C_{12}H_{13}N_3$ Mol. Wt. 199.25 Beil. Ref. XIII, 110

$H_2N—C_6H_4—NH—C_6H_4—NH_2$

Use: Detection of hydrogen cyanide.

p-Diaminodiphenylamine is obtained as crystalline leaves from water. It melts at 157-158° C.

Preparation: *p*-Diaminodiphenylamine is prepared by mixing an ice-cold, neutral solution of *p*-phenylenediamine and aniline with potassium dichromate. A blue oxidation product is obtained, which on warming with zinc and hydrochloric acid yields *p*-diaminodiphenylamine.[1]

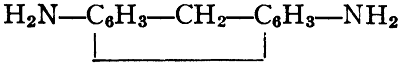
The reagent may also be prepared by dissolving 23.5 g. of finely powdered 4-aminoazobenzene hydrochloride in 350-400 ml. of a saturated aqueous solution of sulfur dioxide, and adding with shaking 15 g. of zinc. When the mixture is completely decolorized, pour into 100 g. of 50 per cent sulfuric acid. Heat to boiling and allow to stand for 24 hours. Collect the crystals and dry, and then wash several times with small quantities of water. To convert the sulfate to the free base, boil with a small excess of sodium carbonate. Crystallize from boiling water.[2]

Detection of hydrogen cyanide. Peset and Aguilar[3] have used *p*-diaminodiphenylamine to replace tincture of guaiac in the well-known test for hydrogen cyanide. A piece of filter paper which has been dipped in a solution of *p*-diaminodiphenylamine and moistened with copper sulfate is colored a light bluish-green when suspended in a gas containing hydrogen cyanide.

1. R. Nietzki, *Ber.* **16**, 474 (1883).
2. P. Barbier and P. Sisley, *Bull. soc. chim.* [3] **33**, 1233 (1905).
3. J. Peset and J. Aguilar, *Arch. med. legal* (*Portugese*). **1**, 18-21 (1922); *C.A.* **17**, 3149 (1923).

2,7-DIAMINOFLUORENE

$C_{13}H_{12}N_2$ Mol. Wt. 196.23 Beil. Ref. XIII, 266(85)



$H_2N—C_6H_3—CH_2—C_6H_3—NH_2$

Uses: Detection of bromide, cadmium, chloride, cobalt, copper, nitrate, persulfate, and zinc.

Determination of zinc.

2,7-Diaminofluorene is obtained as needles by crystallizing from water. It melts at 165° C. It is only very slightly soluble in cold water, but is more soluble in hot water, and is readily soluble in alcohol. 2,7-Diaminofluorene hydrochloride is a crystalline solid which dissolves readily in hot water.

Preparation: Add in small portions 10 g. of fluorene to 200 ml. of a mixture of equal parts of nitric acid (d = 1.52) and glacial acetic acid. Cool at first so that the temperature does not rise appreciably above 60° C. When the reaction is complete, filter, and recrystallize the product twice from hot acetic acid. The product is 2,7-dinitrofluorene.

Triturate 11 g. of the crystals with 350 ml. of concentrated hydrochloric acid, and add 44.3 g. of granulated tin and heat on a water-bath. After about 1 hour, when all the tin has dissolved, boil with 500 ml. of water and filter. On long standing white needles separate from the filtrate. Filter and wash the residue with cold 20 per cent hydrochloric acid. These crystals consist of a double salt of 2,7-diaminofluorene with tin. Dissolve this compound in water and saturate with hydrogen sulfide. Filter off the precipitate of tin sulfide and evaporate the filtrate to obtain crystals of 2,7-diaminofluorene hydrochloride. An aqueous solution of this salt gives a white precipitate of the free base when treated with ammonium hydroxide.[1,2]

Detection of zinc, cadmium and copper. In the presence of sodium chloride, zinc, and cadmium salts yield white precipitates with 2,7-diaminofluorene, and copper yields a blue precipitate or a blue-green solution. By means of these reactions copper, cadmium and zinc may be detected.[1,2]

Determination of zinc. The following procedure for the determination of zinc is recommended by Nino and Calvet:[2]

Procedure. Add 50 ml. of 96 per cent alcohol to 25 ml. of a solution of zinc chloride containing 0.2-0.6 per cent of zinc. Heat to 40-45° C., and add dropwise 30 ml. of a 1 per cent alcoholic solution of 2,7-diaminofluorene. Allow to stand 3-4 hours at room temperature and filter. Wash with 75 ml. of alcohol, and then with 50 ml. of ether. Dry at 90° C. and weigh. The factor for zinc in this precipitate is 0.197.

Results obtained with this method agree very closely with those obtained by Ball and Agruss.[3] Aluminum and zinc cannot be separated by the use of 2,7-diaminofluorene. The above method cannot be applied to the determination of cadmium.[9]

Detection of cobalt. Folcini[4] and Brau[5] have suggested the use of 2,7-diaminofluorene instead of tolidine or benzidine in the Chiarottino[6] reaction for cobalt using dimethylglyoxime.

Detection of chlorine, bromine and persulfate. An aqueous solution of 2,7-diaminofluorene is unchanged by air or nitric acid, but chlorine immediately produces a color ranging from blue, through green to yellow, depending upon the concentration of chlorine. As little as 0.00017 mg. of chlorine per ml. can be detected by this method. This reaction is much more sensitive than that employing benzidine, which yields a color only with 3 times as much chlorine.

Potassium persulfate is detected in a similar reaction at a dilution of 1:1,000,000 within 5 minutes.[7]

Detection of nitrates. A solution of 2,7-diaminofluorene or 2,7-diaminofluorene hydrochloride in concentrated sulfuric acid is a very sensitive reagent for the detection of nitrates. A 0.1 per cent solution of 2,7-diaminofluorene in sulfuric acid is brown in color, and a solution of the hydrochloride is pale yellow in color. In the presence of as little as 0.001 mg. of potassium nitrate per liter, the solution of the free base gives a distinct yellow color, and a solution of the hydrochloride yields a greenish-yellow color. The test is carried out as follows:[8]

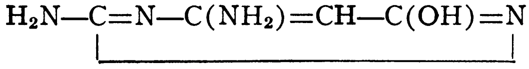
Procedure. To 1 ml. of an aqueous solution of an alkali nitrate, add 5 ml. of concentrated sulfuric acid and cool with running water. Add 2-3 drops of a 1 per cent solution of 2,7-diaminofluorene or 2,7-diaminofluorene hydrochloride in concentrated sulfuric acid. A 0.01 per cent solution of the reagent is recommended with very small quantities of nitrate. Shake well and observe the color.

In case of doubt as to color change, it is best to compare the test solution with a blank.

1. J. Schmidt and W. Hinderer, *Ber.* **64B**, 1793-96 (1931); *C.A.* **25**, 4813 (1931).
2. E. L. Nino and F. Calvet, *Anales soc. espan. fis. quim.* **32**, 698-701 (1934); *C.A.* **28**, 6651 (1934).
3. T. R. Ball and M. Agruss, *J. Am. Chem. Soc.* **52**, 120-4 (1930); *C.A.* **24**, 1316 (1930).
4. A. J. Folcini, *Rev. centro estud. farm. bioquim.* 17, 305-09 (1928); *C.A.* **24**, 2689 (1930).
5. E. F. Brau, *Rev. facultad cienc. quim.* (*Univ. La Plata*). **8**, Pt. 2, 65-70 (1933); *C.A.* **28**, 2641 (1934).
6. A. Chiarottino, *Industria chimica.* **8**, 32 (1933).
7. J. Schmidt and W. Hinderer, *Ber.* **65B**, 87-90 (1932); *C.A.* **26**, 2395 (1932).
8. M. Eitel, *Z. anal. Chem.* **98**, 227-34 (1934); *C.A.* **29**, 71 (1935).
9. K. Heller and F. Machek, *Mikrochemie.* **19**, 147-61 (1936).

2,4-DIAMINO-6-HYDROXYPYRIMIDINE

$C_4H_6ON_4$ Mol. Wt. 126.09 Beil. Ref. XXIV, 469



$$\mathrm{H_2N{-}C{=}N{-}C(NH_2){=}CH{-}C(OH){=}N}$$

Use: Detection of nitrite and nitrate.

Separation of nitrite and nitrate.

2,4-diamino-6-hydroxypyrimidine crystallizes with one molecule of water of hydration. It melts at 286° C. with decomposition.

Preparation: Dissolve 40 g. of guanidine hydrochloride in a little absolute alcohol and mix this solution with 10 g. of sodium, also dissolved in absolute alcohol. Separate the precipitated sodium chloride, and to the liquid add 48 g. of cyanacetic ester. After a time the liquid becomes warm and a precipitate begins to form. Allow to stand 5-6 hours and filter off the crystals of cyanacetylguanidine. 2,4-Diamino-6-hydroxypyrimidine, which is contained in the filtrate, is obtained by evaporation. Purify the product by crystallizing from hot water.[1]

Detection of nitrite. When 2,4-diamino-6-hydroxypyrimidine is added to an aqueous solution containing a soluble nitrite, a strawberry-colored precipitate of 2,4-diamino-5-nitroso-6-hydroxypyrimidine is formed.[2-5] A precipitate is formed with solutions containing as little as 0.05 mg. of nitrite per ml., and a coloration appears with as little as 0.015 mg. per ml.

Efforts to use 2,4-diamino-6-hydroxypyrimidine for the quantitative estimation of nitrites have not been successful. By using the slightly soluble sulfate of the reagent, nitrites may be precipitated from mixtures containing nitrates, and, after filtration, the nitrate may be determined in the filtrate by means of nitron, or it may be detected with the usual reactions employing diphenylamine or ferrous sulfate. The sulfate is used for the precipitation, since an excess of this reagent largely crystallizes out in the cold, and is removed by filtration. Consequently it does not interfere with the nitrate determination or detection.[2]

In the filtrate obtained after precipitating nitrite with 2,4-diamino-6-hydroxypyrimidine, as little as 0.002 mg. of nitrate per ml. may be detected.[6]

Detection of nitric acid and nitrates. Nitrates may be detected by means of a characteristic coloration formed with 2,4-diamino-6-hydroxypyrimidine in the presence of sulfuric acid.[7]

Procedure. In a test tube place 1 ml. of a 10 per cent aqueous solution of 2,4-diamino-6-hydroxypyrimidine (base) or one of its salts, and add an equal volume of the solution to be tested. Carefully pour 3 ml. of concentrated sulfuric acid down the side of the tube so as to form two liquid layers. A red color develops at the junction of the two liquids if nitrate is present. On shaking the color deepens and spreads throughout the entire solution.

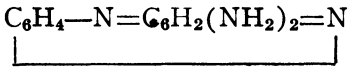
The above test is obtained with 0.5 mg. of nitrate, and in the presence of other anions, but the temperature must not exceed 30° C. when sulfur dioxide is present. Chlorate, bromide and iodide interfere, but if sulfurous acid is added to solutions containing these ions, the test for nitrate is obtained. The reagent also gives a reaction with nitrites, but the characteristic color of the nitrate does not appear.

The nitrate test with 2,4-diamino-6-hydroxypyrimidine is not as delicate as the ferrous sulfate ring test, but it possesses the advantage over the latter that other anions, even nitrites, do not cause serious interference.

1. W. Traube, *Ber.* **33**, 1371 (1900).
2. F. L. Hahn, *Ber.* **50**, 705-8 (1917); *J. Chem. Soc.* **112**, II 382; *C.A.* 11, 3195 (1917).
3. F. L. Hahn, *Mikrochemie, Emich Festschr.* 143-7 (1930); *C.A.* **25**, 3272 (1931).
4. F. L. Hahn, *Mikrochemie.* **9**, 31 (1931).
5. F. L. Hahn, *Z. anal. Chem.* **62**, 470 (1923).
6. F. L. Hahn and P. Baumgarten, *Ber.* **63B**, 3028-9 (1930); *C.A.* **25**, 894 (1931).
7. H. Wolf and E. Heymann, *Z. angew. Chem.* **37**, 195-6 (1924); *C.A.* **18**, 2661 (1924).

2,3-DIAMINOPHENAZINE

$C_{12}H_{10}N_4$ Mol. Wt. 210.20 Beil. Ref. XXV, 389(652)



$C_6H_4{-}N{=}C_6H_2(NH_2)_2{=}N$

Use: Detection of bismuth, cadmium, cupric, lead, and mercuric ions.

2,3-Diaminophenazine consists of brown-yellow needles. It sublimes by careful heating to yellow leaves. It dissolves in alcohol and benzene with a greenish-yellow fluorescence. Alcoholic solutions of salts of the compound fluoresce dark orange-red.

Preparation: Dissolve 3.6 g. of *o*-phenylenediamine in 100 ml. of water, and to this solution add slowly and in small portions 4 ml. of 40 per cent ferric chloride solution with vigorous shaking and cooling with water. Allow to stand 3-4 hours and filter off the dark brown crystals with suction. Wash with a little dilute hydrochloric acid and dry on a water-bath. Dissolve the crystals in 150 ml. of water, and decompose at the boiling point with dilute sodium hydroxide to a strongly alkaline reaction. Filter, wash the diaminophenazine crystals with water and dry.[1]

Reactions. An ethyl alcohol solution of the reagent yields yellow or orange precipitates with bismuth, lead, and cadmium, and red precipitates with mercuric and cupric ions.[2,3] Bismuth, lead, and cadmium do not give characteristic colors in dilute solutions, but the reactions with mercury and copper are very sensitive. Mercury can be detected at a dilution of 1:100,000, and copper at a dilution of 1:6 million.

Procedure. Neutralize the solution to be tested with sodium hydroxide, and add 2-3 drops of an alcoholic solution of the reagent with vigorous stirring. The color appears first in the froth formed by stirring, but it gradually settles.

Iron and ammonium ions interfere and must be removed before making test.

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1. F. Ullmann and F. Mauthner, *Ber.* 35, 4307 (1902).
2. T. Pavolini, *Industria Chimica.* 8, 692-4 (1933) ; *C.A.* 27, 5270 (1933).
3. K. Heller and F. Machek, *Mikrochemie.* 19, 147-61 (1936).

DIANISIDINE

Synonym: 3,3′-Dimethoxybenzidine

$C_{14}H_{16}O_2N_2$ Mol. Wt. 244.28 Beil Ref. XIII, 807

$$H_2N(CH_3O)C_6H_3—C_6H_3(CH_3O)NH_2$$

Uses: Detection of cobalt, copper, gold, thiocyanate and vanadium.

Determination of gold and nitrite.

Dianisidine consists of colorless or white crystals which turn violet on standing. It melts at 137-138° C. It is insoluble in water, but dissolves in alcohol, benzene and ether.

Preparation: Dianisidine is prepared by suspending 2,2′-dimethoxyazobenzene in aqueous hydrochloric acid, and reducing with sulfurous acid and iodine.[1]

Detection of vanadium. Vanadium catalyzes the reaction between dianisidine and potassium periodate, and as a result of this activity as little as 0.1γ of vanadium can be detected. This reaction, however, is of little value, since many ions interfere.[2,3]

Reagents. *Dianisidine solution.* A 0.05 per cent solution of dianisidine hydrochloride.

8-Hydroxyquinoline solution. A 1 per cent solution of 8-hydroxyquinoline in N acetic acid.

Procedure. Mix 0.2 ml. of dianisidine solution, 0.3 ml. of 8-hydroxyquinoline solution, and 0.1 ml. of a saturated potassium periodate solution, and dilute to 5 ml. Simultaneously prepare a comparison blank. After a time a red color gradually appears, and suddenly the red dye precipitates and the solution becomes turbid. In the presence of vanadium the reaction proceeds much more rapidly than in its absence.

The reaction is made much more sensitive by the presence of 8-hydroxyquinoline.

Detection and determination of gold. Auric gold reacts with *o*-dianisidine in a weakly acid solution to form a red color. The amine has been used as an indicator in a titrimetric method for determining gold,[9,10] and for the colorimetric determination of small quantities of gold.[11]

Procedure. To approximately 50 ml. of sample containing a few drops of mineral acid, add 0.5 ml. of 5 per cent potassium bifluoride and 0.1 ml. of 0.1 per cent *o*-dianisidine in 0.05 N hydrochloric acid. The color is compared after 10-15 minutes.

Chlorine, bromine and nitrosyl chloride must be absent.

This method may be used for the determination of gold in biological fluids after destruction of the organic matter with sulfuric acid and hydrogen peroxide, and oxidation of gold with aqua regia.

Detection of cobalt. Brau[4] has used dianisidine in the place of benzidine in Chiarottino's[5] test for cobalt.

Detection of copper and thiocyanate. Spacu's[6] reaction for copper is improved by substituting various polysulfides for the thiocyanate (page 284). Dianisidine may be used in place of tolidine or benzidine in this reaction.[7]

Determination and detection of nitrites in water. Primot[8] has used dianisidine for the colorimetric determination of nitrites in water.

Procedure. Add 5 drops of a 1-1.5 per cent solution of dianisidine in 30-40 per cent alcohol, and 5 drops of acetic acid to 10 ml. of water under examination. If nitrite is present, a yellow color appears, and this becomes orange-red on standing. The maximum intensity is reached after about 30 minutes. As little as 0.01 g. of nitrous acid in 1 liter gives this reaction. Sulfates and free mineral acids interfere with this reaction and must be removed.

Nitrous acid may be determined colorimetrically by comparing the color produced in above reaction with that obtained using solutions of known nitrite concentration.

1. *Chem. Zentr.* **II**, 479 (1906).
2. L. Szebelledy and M. Ajtai, *Mikrochemie.* **26**, 75-86 (1939) ; *C.A.* **33**, 3290 (1939).
3. L. Szebelledy and M. Ajtai, *Magyar Gyogyszeresztud Tarsasag Ertesitoje.* **14**, 560-77 (1938) ; *C.A.* **32**, 8986 (1938).
4. E. F. Brau, *Rev. facultad cienc. quim.* (*Univ. La Plata*). **8**, Pt. 2, 65-70 (1933) ; *C.A.* **28**, 2641 (1934).
5. A. Chiarottino, *Industria chimica.* **8**, 32-33 (1933) ; *C.A.* **27**, 2396 (1933).

6. G. Spacu and C. G. Macarovici, *Z. anal. Chem.* **102**, 350-2 (1935); *C.A.* **30**, 43 (1936).
7. A. J. Folcini, *Rev. centro estud. farm. bioquim.* **17**, 305-9 (1928); *C.A.* **24**, 2689 (1930).
8. M. Primot, *Bull. sci. pharmacolog.* **19**, 546 (1912); *C.A.* **7**, 1069 (1913).
9. W. B. Pollard, *Analyst.* **62**, 597 (1937).
10. A. R. Jamieson and R. S. Watson, *Analyst.* **63**, 702 (1938).
11. W. D. Block and O. H. Buchanan, *J. Biol. Chem.* **136**, 379 (1940).

DIBENZYLAMINE

$C_{14}H_{15}N$ Mol. Wt. 197.27 Beil. Ref. XII, 1035(453)

$$C_6H_5—CH_2—NH—CH_2—C_6H_5$$

Use: Detection of cobalt, cyanate and iron.

Dibenzylamine is a colorless oil having an ammoniacal odor. It boils at 300° C. with partial decomposition. It is insoluble in water, but dissolves readily in alcohol and ether.

Preparation: Dibenzylamine is prepared by the action of alcoholic ammonia on benzyl chloride.[1]

Detection of cobalt, cyanate and iron. Dibenzylamine may be used in place of pyridine in reactions between cyanates and cobalt or iron.[2] For details of the test, see section on pyridine.

1. A. T. Mason, *J. Chem. Soc.* **63**, 1312 (1893).
2. R. Ripan, *Bull. soc. stiinte Cluj.* **4**, 144 (1928).

DICHLOROBENZIDINE

Use: Detection of gold.

Detection of gold. Frierson and Simpson[1] report that dichlorobenzidine gives a green color with gold. This reaction is sensitive to about one part in five million. No information is given as to which of the isomeric dichlorobenzidines (Beil. Ref. XIII, 234, 66, 67) was used.

1. W. J. Frierson and P. M. Simpson, *Va. J. Sci.* **3**, 11 (1942).

DIETHANOLAMINE

$C_4H_{11}O_2N$ Mol. Wt. 105.14 Beil. Ref. IV, 283

$$CH_2OH—CH_2—NH—CH_2—CH_2OH$$

Use: Detection and determination of copper.

Diethanolamine consists of colorless or white crystals which liquefy and fume strongly in moist air. It melts at 28° C., and boils at 268° C., and has a sp. gr.

of 1.08. It is a strong base. It is soluble in water and is miscible with alcohol and hot acetone, but is insoluble in ether or benzene.

Preparation: Diethanolamine is produced along with mono- and triethanolamine by the action of ethylene oxide on an excess of cold concentrated ammonia.[1]

Detection and determination of copper. Pozzi-Escot[2] has proposed a sensitive test for copper based on the color which is obtained when a solution of a copper salt is made alkaline with diethanolamine and then saturated with carbon dioxide.

1. A. Wurtz, *Ann.* 121, 228 (1862).
2. E. Pozzi-Escot, *Rev. cienc* (*Peru*). **39**, No. 421, 31-4 (1937); *C.A.* **32**, 2048 (1938).

DIETHYLAMINE

$C_4H_{11}N$ Mol. Wt. 73.14 Beil. Ref. IV, 95

$$C_2H_5—NH—C_2H_5$$

Uses: Determination of carbon disulfide and magnesium.

Detection of antimony, platinum metals, and tin.

Diethylamine is a colorless, inflammable, strongly alkaline liquid. It has a sp. gr. of 0.711, and boils at 55.5° C. It is miscible with water and alcohol, and is usually obtained in the form of a solution.

Preparation: Dissolve 50 g. of diethylaniline in 148 g. of hydrochloric acid (d = 1.12), dilute the mixture with 75 ml. of water, and add with cooling a solution of 32 g. of sodium nitrite in 50 ml. of water. Pour this mixture slowly into a boiling solution of 85 g. sodium hydroxide in 2 liters of water. Boil 45 minutes and collect the separated diethylamine in dilute hydrochloric acid.[1]

Determination of carbon disulfide in air. Carbon disulfide in air may be determined by a method based upon the formation of a yellow or golden-brown coloration by the action of carbon disulfide on diethylamine in the presence of copper ions.[2-6] The color obtained in an alcohol solution fades rather rapidly, but the color is more intense and more stable when produced in methyl cellosolve as a reaction medium. This method is more sensitive and more accurate than that based on the formation of xanthate. The xanthate method also requires large volumes of air (2 cubic feet or more).

Detection of tin and antimony. Gautier[7] has used diethylamine for the detection of tin and antimony. A reagent consisting of 2 g. of potassium iodide and 1 g. of diethylamine dissolved in sufficient water to make 30 ml. of solution gives a yellow to orange-yellow precipitate with antimony chloride, and a white to yellowish-white precipitate with stannous chloride.

Detection of the platinum metals. Whitmore and Schneider[9] have studied the use of diethylamine hydrochloride as a reagent for the microdetection of the platinum metals. This compound has proved particularly useful for the detection of platinum. The following procedure is used:

Procedure. Place a drop of the solution to be tested on a glass slide, and evaporate to dryness by gentle warming. Pass a narrow streak of a 10 per cent solution of diethylamine hydrochloride over the dried film. Bright yellow crystals form immediately if platinum is present. Many of these are diamond-shaped, flat plates. Short hexagonal prisms with beveled ends, and octahedra with truncated apices also may be observed. This test may be modified by evaporating the solution with a fragment of the solid reagent.

The reactions of the platinum metals with diethylamine hydrochloride are summarized in Table 41, which is taken from the work of Whitmore and Schneider:

TABLE 41.—REACTION OF PLATINUM METALS WITH DIETHYLAMINE HYDROCHLORIDE

Test Material 2% Solution

Reagent Diethylamine Hydrochloride—Solid Fragment

Test Material	Description
$RuCl_3$	No apparent reaction.
$RhCl_3$	No apparent reaction.
$PdCl_2$	On standing for some time some irregular crystalline structures form around the edge of the drop. If these are broken up and pushed into the drop many crystalline forms appear. These are hexagonal and diamond shaped flat plates of a pale purple color.
Na_2OsCl_6	On standing for some time bright-yellow, diamond shaped plates, hexagonal plates and short hexagonal prisms with beveled ends appear.
$IrCl_4$	On standing some time many, deep red, diamond-shaped plates appear. Some deep-red short hexagonal prisms also appear.
H_2PtCl_6	Many bright-yellow rhombs are formed immediately. There also appear short hexagonal prisms and some cubic forms. .
$AuCl_3$	Very long, bright-yellow, needle-shaped crystals develop around the edge of the drop. These gradually develop throughout the drop.

Precipitation of magnesium. Hemming[8] has used diethylamine for the precipitation of magnesium, zinc and other metals, but he reports that better results are obtained by using guanidine as the precipitant.

1. J. F. Norris and A. E. Kimberly, *Am. Chem. J.* 20, 60.
2. F. F. Morehead, *Ind. Eng. Chem., Anal. Ed.* 12, 373 (1940).
3. T. Callan, J. R. Henderson, and J. Stafford, *J. Soc. Chem. Ind.* 51, 193-4T (1932).
4. L. W. Conn, A. J. Johnson, H. A. Trebler, and V. Karpenko, *Ind. Eng. Chem., Anal. Ed.* 7, 15-23 (1935).
5. *Dept. Sci. Ind. Research,* Leaflet 6, London, Eng. Stationery Office (1939).

6. N. Tishler, *Ind. Eng. Chem., Anal. Ed.* **4**, 146 (1932).
7. J. A. Gautier, *J. pharm. chim.* **23**, 283 (1936).
8. G. Hemming, *Z. anorg. Chem.* **130**, 333 (1923); *C.A.* **18**, 799 (1924).
9. W. F. Whitmore and H. Schneider, *Mikrochemie.* **17**, 279-319 (1935).

DIETHYLANILINE

$C_{10}H_{15}N$ Mol. Wt. 149.23 Beil. Ref. XII, 164

$C_6H_5N(C_2H_5)_2$

Use: Detection of manganese and zinc.

Diethylaniline is a colorless to yellow liquid. It boils at 215-216° C. and melts at −38°. Its sp. gr. is 0.935. It is slightly soluble in alcohol, ether, and chloroform.

Preparation: Mix 130 g. of dried aniline hydrochloride and 140 g. of 95 per cent ethyl alcohol, and heat in an enameled autoclave at 180° C. for 8 hours. Cool, and transfer the mixture to a round-bottomed flask, and distill off the alcohol and ether. Add 110 g. of 30 per cent sodium hydroxide solution to the residue. Stir the mixture at room temperature with 40 g. of *p*-toluenesulfonchloride, which forms a non-volatile derivative of monoethylaniline. Steam distill the diethylaniline. Salt out the amine with sodium chloride, separate, and distill.[1]

Detection of zinc. Alkali ferricyanides are capable of oxidizing diethylaniline, as well as other aromatic amines and certain monoazo dyes, with consequent noticeable color changes and the formation of ferrocyanides. Normally the oxidation proceeds slowly, but if the ferrocyanide is removed by zinc ions as insoluble zinc ferrocyanide, the reaction proceeds rapidly. Since the precipitated zinc ferrocyanide is deeply colored by the oxidation product of the amine or dye, this reaction constitutes a sensitive test for zinc. This test is particularly useful in a systematic scheme of analysis, since chromium and aluminum do not interfere. Traces of iron do not interfere, although cobalt, nickel, manganese, and copper form colored precipitates.

A phosphoric acid solution of diethylaniline is pale yellow in color, but this color changes to brown or red when potassium ferricyanide and a little zinc salt are added. In concentrated sulfuric acid, the reagent is dark yellow, and this color changes to brownish-red, and a precipitate forms when potassium ferricyanide and zinc are added. These color changes have been used as a test for zinc by Eegriwe.[2]

Method 1

Reagents. *Potassium ferricyanide solution.* Dissolve 2 g. of potassium ferricyanide in 100 ml. of water.

Diethylaniline solution. Dissolve 0.5 ml. of diethylaniline (mono-free) in 200 ml. of 50 per cent phosphoric acid.

Procedure. Add 0.3 ml. of the diethylaniline solution to 0.25 ml. of the potassium ferricyanide solution, and then add 1 drop of the slightly acid solution to be tested. A brownish-yellow to brownish-red color indicates zinc.

Method 2

Reagents. *Potassium ferricyanide solution.* Dissolve 2 g. of potassium ferricyanide in 100 ml. of water.

Diethylaniline solution. Dissolve 25 ml. of diethylaniline (mono-free) in 200 ml. of cold 1:1 sulfuric acid.

Procedure. Mix 0.75 ml. of the potassium ferricyanide solution with 0.5 ml. of the diethylaniline solution, and add 1 drop of the solution to be tested. The orange-colored reagent turns to a reddish-brown, and a turbidity forms if zinc is present. As little as 0.01 mg. of zinc gives this test.

This test has been used for the detection of zinc in a systematic scheme of analysis.[3,4]

Detection of manganese. Small quantities of manganese may be detected by its catalytic effect in promoting the oxidation of diethylaniline by potassium periodate. In this way as little as $10^{-5}\gamma$ of manganese can be detected at a concentration limit of 1:5 x 10^{11}. This reaction is similar to those used by Szebelledy for the detection of vanadium.[5]

1. St. v. Niementowski, *Ber.* **30**, 3072 (1897).
2. E. Eegriwe, *Z. anal. Chem.* **74**, 225-31 (1928); *C.A.* **22**, 3859 (1928).
3. T. Grosset, *Ann. soc. Bruxelles.* **53B**, 16-41 (1933); *C.A.* **27**, 2902 (1933).
4. B. Tougarinoff, *Ann. soc. sci. Bruxelles.* **50**, Ser. B 145-246 (1930); *C.A.* **25**, 1456 (1931).
5. L. Erdey, *Kem. Lapja* **3**, 45-7, 65-7 (1942); *C.A.* **38**, 6228 (1944).

N-DIETHYLBENZOHYDRYLAMINE

$C_{17}H_{21}N$ Mol. Wt. 239.34

$(C_2H_5)_2N—CH(C_6H_5)_2$

Use: Detection of nitrate.

N-Diethylbenzohydrylamine is a solid melting at 58-59° C.

Preparation: Mix the calculated quantities of benzohydrylamine and ethyl bromide with a concentrated solution of potassium carbonate, and heat 6-8 hours in a sealed tube immersed in boiling water. The resulting mixture, of benzohydrylamine, mono- and diethylbenzohydrylamine is separated by the usual method of amine separation. Benzohydrylamine is converted to the carbonate by treating with carbon dioxide. The mono- and diethylbenzohydrylamines are separated by reacting with nitrous acid and treating with ether.

Detection of nitrate. *N*-Diethylbenzohydrylamine forms a nitrate which is only slightly soluble in water. A 0.017 M solution of potassium nitrate yields a precipitate when treated with a saturated aqueous solution of the reagent. To test for nitrate in the presence of nitrite in a solution from which all other anions have been removed, proceed as follows:[1]

Procedure. Concentrate the solution by evaporation and add 1 drop of a saturated solution of *N*-diethylbenzohydrylamine hydrochloride. Rub the sides of the test tube with a glass rod if a precipitate does not form immediately. If a turbidity appears, add 1-1.5 ml. of water. If the precipitate does not dissolve immediately nitrate is present.

Hydrogen iodide and perchloric acid in concentrations as low as 0.002 M form precipitates with *N*-diethylbenzohydrylamine and must be absent. *N*-Diethylbenzohydrylamine is said to be more satisfactory than nitron for the detection of nitrate, since the latter precipitates both nitrite and nitrate. *N*-Diethylbenzohydrylamine forms a more soluble nitrite.

1. A. Ogata and M. Konishi, *J. Pharm. Soc. Japan.* 54, 546-50 (1934); *C.A.* **31**, 63 (1937).
2. M. Sommelet, *Compt. rend.* 175, 1149-51 (1922).
3. M. Sommelet and M. Guioth, *Compt. rend.* 174, 687 (1922).

s-DIETHYLDIPHENYL UREA

$C_{17}H_{20}ON_2$ Mol. Wt. 268.33 Beil. Ref. XII, 422

$$C_2H_5(C_6H_5)N{-}CO{-}N(C_6H_5)C_2H_5$$

Use: Detection of nitrate and nitrite.

s-Diethyldiphenyl urea is obtained as a crystalline solid from alcohol. It melts at 79° C. and is insoluble in water.

Preparation: *s*-Diethyldiphenyl urea is prepared by saturating ethylaniline with phosgene gas, mixing with an equal volume of ethylaniline, and heating the mixture for 1 hour at 130° C. Purify with water and hydrochloric acid, from which crystals of the reagent separate on evaporation.[1]

Color reaction for nitrous and nitric acids. *s*-Diethyldiphenyl urea reacts with traces of nitrates and nitrites in a sulfuric acid solution to give a currant-red color.[2]

Procedure. Mix 1 ml. of the solution to be tested with a little *s*-diethyldiphenyl urea in a test tube, and then pour 1 ml. of concentrated sulfuric acid down the side of the tube. As little as 1 part of nitric acid in 250,000 parts of water gives a perceptible color reaction.

Other oxidizing agents such as chlorates and chromates also give this reaction.

1. W. Michler, *Ber.* 9, 712 (1876).
2. L. Desvergnes, *Ann. chim. anal. chim. appl.* 6, 102-3 (1924); *C.A.* 18, 1799 (1924).

DIMETHYLAMINE

C_2H_7N Mol. Wt. 45.08 Beil. Ref. IV, 39

$CH_3—NH—CH_3$

Use: Determination of magnesium and zinc.

Dimethylamine is a gas at ordinary temperatures. It is very soluble in water, with which it forms a very strongly alkaline solution. It is also soluble in alcohol and ether. It is usually marketed as a liquid under pressure, or as a 33 per cent aqueous solution.

Preparation: Mix 100 g. of ammonium chloride and 200 ml. of a 40 per cent formaldehyde solution in a 1-liter distilling flask attached to a long condenser. Heat gradually until a thermometer immersed in the liquid registers 104° C. Maintain the temperature at 104° C. for about 4-5 hours, or until no more liquid passes over, and then allow the contents of the flask to cool. Filter off the crystals of ammonium chloride and add an additional 150 ml. of formaldehyde to the filtrate and pour the mixture back into the distilling flask. Again heat, this time to 115° C., until no more liquid distills over. This requires about 3.5 hours. Concentrate the product on a water-bath until a scum forms on the surface of the liquid, and then allow to cool. Remove the ammonium chloride and methylamine hydrochloride by filtration. Heat the filtrate to 120° C. until a sample of the liquid on cooling becomes semi-solid. Allow the mixture to cool, and place in a vacuum desiccator over solid sodium hydroxide, and allow to stand for two days. Digest the residue with chloroform for a time, and then filter. On cooling, dimethylamine hydrochloride crystallizes from the chloroform extract.[1,2] The free amine is obtained by treating the salt with sodium hydroxide.

Determination of magnesium, zinc and other metals. Dimethylamine has been used by Hemming[3] and Borgstrom[4] for the precipitation of magnesium, zinc and other metals. Results obtained using guanadine, piperidine, sodium hydroxide, tetramethylammonium hydroxide, and tetraethylammonium hydroxide appear to be more satisfactory as precipitants for magnesium than dimethylamine, although the latter is said to give good results.

1. P. Knudsen, *Ber.* 47, 2694 (1914).
2. E. A. Werner, *Trans. Chem. Soc.* **111**, 850 (1917).
3. G. Hemming, *Z. anorg. Chem.* **130**, 333 (1923); *C.A.* **18**, 799 (1924).
4. L. H. Borgstrom, *Hyllningsskrift tillagnad Ossian Aschan.* 118-23 (1920); *C.A.* **16**, 2091 (1922).

p-DIMETHYLAMINOBENZYLIDENEBENZIDINE

$C_{30}H_{30}N_4$ Mol. Wt. 446.54 Beil. Ref. XIV, 35

$(CH_3)_2N—C_6H_4—CH=N—C_6H_4—C_6H_4—N=CH—C_6H_4—N(CH_3)_2$

Use: Determination of tungsten.

p-Dimethylaminobenzylidenebenzidine is a yellow crystalline solid which melts at 318° C.

Preparation: Mix 2 g. of hydrazobenzene and 3.2 g. of *p*-dimethylaminobenzaldehyde in 30 ml. of acetic acid and boil for 2.5 hours under reflux. Cool and add water until a faint turbidity appears, and then allow to stand for a short time and filter. Make the filtrate alkaline with ammonium hydroxide, filter off the precipitated reagent, and crystallize from boiling benzene.[1]

Determination of tungsten. *p*-Dimethylaminobenzylidenebenzidine reacts with solutions of alkali tungstates to give a cinnabar-red precipitate. This precipitate is converted to WO_3 upon ignition. Precipitation is quantitative, but the compound is slightly soluble in water and must be washed with a dilute solution of the precipitant. The precipitate is very voluminous and is very difficult to wash and filter. For this reason *p*-dimethylaminobenzylidenebenzidine is less satisfactory as a precipitant for tungsten than vanillylidenebenzidine.

1. F. Sachs and C. M. Whittaker, *Ber.* **35**, 1435 (1902).
2. V. Hovorka, *Collection Czechoslov. Chem. Commun.* **10**, 518-26 (1938); *C.A.* **33**, 1624 (1939).

DIMETHYLANILINE

$C_8H_{11}N$ Mol. Wt. 121.18 Beil. Ref. XII, 141

$C_6H_5—N(CH_3)_2$

Uses: Detection of hydrogen peroxide, hydrogen sulfide, nickel and nitrite.

Determination of cerium, lanthanum, neodymium, nitrite, praseodymium, thorium and zirconium.

Dimethylaniline is a yellowish to brown colored, oily liquid. It boils at 192-194° C., and has a sp. gr. of 0.956. It is insoluble in water, but is freely soluble in alcohol, chloroform and ether.

Preparation: Place 20 g. of aniline in a beaker and add concentrated hydrochloric acid dropwise until a drop of the mixture turns methyl violet paper green. Then quickly cool, stir well, and filter. Place 20 g. of the dry aniline hydrochloride in a thick-walled glass tube, which is closed at one end, and add a mixture of 15 g. of aniline and 22 g. of methyl alcohol. Seal the tube and heat gradually to 150° C. for 2 hours, and then at 180-200° C. for an additional 6 hours. Pour the contents of the tube into a large separatory funnel and add an excess of sodium hydroxide. Add a little ether and remove the upper layer. Extract the lower aqueous portion twice with small quantities of ether, and then dehydrate the ether solution over solid potassium hydroxide. Filter and remove the ether on a water-bath. Boil the residue with 25 g. of acetic anhydride for one hour, using an upright condenser and then distill. Collect the portion boiling at 190-200° C.[1,2]

Precipitation of metals. Zirconium, thorium, cerium, lanthanum, neodymium and praseodymium are precipitated as the hydroxides by treating aqueous solutions of their salts with dimethylaniline.[9]

Detection and determination of nitrite. Nitrites may be detected or determined colorimetrically by means of the yellow color of *p*-nitrosodimethylaniline which is formed when dimethylaniline reacts with a nitrite in an acid solution.[3]

Reagent. Dissolve 8 g. of dimethylaniline and 4 g. of hydrochloric acid in 100 ml. of water.

Procedure. Add 1 drop of concentrated hydrochloric acid and 3 drops of the above reagent to 50 ml. of the solution to be analyzed. A yellow color appears within 15-30 minutes if nitrite is present. By matching the color of the unknown in a colorimeter with that of a standard solution containing sodium nitrite, small quantities of nitrite may be estimated colorimetrically. By means of this reaction 1 part of nitrous acid may be detected in 1,000,000 parts of solution. Nitrates do not interfere.

Sefton[4] has used the above method for detecting nitrite in battery acid, and finds this procedure the most satisfactory of those tested.

A more recent method for detecting nitrite with dimethylaniline, developed by Giblin and Chapman,[5] depends upon the diazotization of sulfanilic acid, followed by couplings with dimethylaniline to form methyl orange.

Reagent. Dissolve 1 g. of dimethylaniline and 1.5 g. of sulfanilic acid in 100 ml. of 0.5 N hydrochloric acid.

Procedure. Add 2 drops of the above reagent to 10 ml. of the solution to be analyzed. A red color appears if nitrite is present.

The intensity of the color formed in the above reaction depends upon time as well as concentration, but with suitable precautions this reaction can be used for the colorimetric determination of nitrites ranging in concentration from 1 to 10 p.p.m.

Detection of hydrogen sulfide. Palet and Fernandez[6] have used dimethylaniline in a modified Fischer reaction for hydrogen sulfide, which depends upon the formation of methylene blue.

Procedure. Add 2 ml. of water, 3-4 drops of 10 per cent solution of sodium nitrite, and 5 drops of 10 per cent hydrochloric acid to a small quantity of dimethylaniline. Stir well, and neutralize the mixture with a cold, saturated solution of sodium carbonate. Extract the resulting nitroso derivatives with ether, and to the latter, after decantation, add a small quantity of zinc and several drops of concentrated hydrochloric acid. Allow the mixture to stand until the green color disappears. Decant the supernatant ether, dilute the remaining liquid with 2 ml. of water, and add the material to be tested for hydrogen sulfide. Next treat the mixture with 1:10 by volume hydrochloric acid and a little ferric chloride according to the Fischer technique (page 252). The reaction may be made more sensitive by extracting the methylene blue with alcohol.

Detection of hydrogen peroxide and chromium. Ilosvay[7] has used dimethylaniline in a sensitive color reaction for hydrogen peroxide.

Reagent. Dissolve 5 drops of dimethylaniline in 0.03 g. of potassium dichromate in 1 liter of water.

Procedure. Mix 5 ml. of the solution to be tested with 5 ml. of the reagent, and add 1 drop of 5 per cent oxalic acid solution. A yellow color appears if hydrogen peroxide is present. One part of hydrogen peroxide may be detected in 5,000,000 parts of water by this reaction.

Detection of nickel. Vincent[8] has suggested the use of dimethylaniline for the detection of nickel, with which it forms an apple-green precipitate.

1. J. B. Cohen, *Practical Organic Chemistry*, 3rd ed., p. 176, Macmillan, London (1937).
2. Poirrier and Chappat, *Jahresb.* 903 (1866).
3. E. H. Miller, *Analyst.* 37, 345 (1912) ; *C.A.* 6, 3380 (1912).
4. L. B. Sefton, *Bur. Standards Tech. Paper.* 149, 10 (1920).
5. J. C. Giblin and G. Chapman, *Analyst.* 61, 686 (1936) ; *C.A.* 31, 68 (1937).
6. L. P. J. Palet and A. Fernandez, *Anales. soc. quim., Argentina.* 6, 49-51 (1918) ; *C.A.* 13, 104 (1919).
7. L. Ilosvay, *Ber.* 28, 2029 (1895).
8. C. Vincent, *Z. Anal. Chem.* 19, 480 (1880) ; *Bull. soc. chim.* 46, 287 (1886).
9. A. M. Jefferson, *J. Am. Chem. Soc.* 24, 540-62 (1902).

DIMETHYL-α-NAPHTHYLAMINE

$C_{12}H_{13}N$ Beil. Ref. XII, 1221

Mol. Wt. 171.23

$C_{10}H_7—N(CH_3)_2$

Uses: Detection of nitrite.

Determination of nitrite.

Dimethyl-α-naphthylamine is an aromatic, colorless oil. It boils at 272-4° C., and possesses a weak, violet fluorescence. It is readily soluble in alcohol and ether.

Preparation: Dissolve 1 gram-molecular weight of α-naphthylamine in methyl alcohol and add 2 gram-molecular weights of methyl iodide, and then heat for one day in a closed tube at 100° C. Open the tube and evaporate the excess alcohol and methyl iodide on a water bath. Decompose the reaction product with sodium hydroxide and shake out with ether. Acidify the ether extract with dilute sulfuric acid to precipitate the α-naphthylamine. Decompose the sulfuric acid with sodium hydroxide, and again extract with ether. Dry with solid potassium hydroxide and distill. Collect the fraction boiling at 267° C.[1]

Detection and determination of nitrites. Germuth[2] recommends the use of dimethyl-α-naphthylamine in place of α-naphthylamine in the usual test for nitrites (page 404). According to his investigations dimethyl-α-naphthylamine produces a more stable and distinct coloration than α-naphthylamine in solutions containing small quantities of nitrite. As a reagent in water analysis use a solution containing 5.25 g. of amine dissolved in a liter of 4 N acetic acid in 95 per cent methanol. This reagent is stable and of high sensitiveness. It is used with sulfanilic acid in the usual manner.

1. L. Landshoff, *Ber.* 11, 643 (1878).
2. F. G. Germuth, *Ind. Eng. Chem., Anal. Ed.* 1, 28-9 (1929); *C.A.* 23, 1079 (1929).

β-DINAPHTHYLAMINE

$C_{20}H_{15}N$ Mol. Wt. 269.33 Beil. Ref. XII, 1278

$C_{10}H_7—NH—C_{10}H_7$

Use: Detection of chlorate, nitrate, and nitrite.

β-Dinaphthylamine is obtained as glistening silvery leaves from benzene. It melts at 170.5° C. It is slightly soluble in boiling alcohol and is very easily soluble in boiling glacial acetic acid.

Preparation: Heat β-naphthol with twice its weight of zinc chloride-ammonia in an oil-bath at 200-210° C. Zinc ammonia chloride is prepared by passing a current of dry ammonia gas into molten zinc chloride or over pulverized anhydrous zinc chloride. The reaction products separate into two layers, one of which is yellow and the other gray. Boil the gray crystalline mass with hydrochloric acid and then with sodium hydroxide. The gray residue is moderately soluble in hot benzene from which crystals separate on cooling. Wash with benzene and then with alcohol, and finally recrystallize the almost white leaves from benezene.[1]

The amine may also be prepared from β-naphthylamine as follows: Mix 100 g. of β-naphthylamine with 0.5 g. of iodine and heat ot 230° C. for 4 hours. Cool the mass and recrystallize from benzene.

Detection of nitrite, nitrate and chlorate. A solution of β-dinaphthylamine in sulfuric acid reacts with nitrates to give a brownish-green color; with nitrites to give an olive-green color; and with chromates to give a brownish-violet color. Chlorates, however, react with this reagent to give a violet color. These reactions have been used by Sa [2] for the detection of nitrites, nitrates and chlorates. The test is carried out in exactly the same manner as described in the section on β-naphthylphenylamine. The sensitivities of the two reactions are about the same.

1. V. Merz and W. Weith, *Ber.* 13, 1300 (1880).
2. H. Sa, *Anales farm. bioquim.* 5, 111-4 (1934); *C.A.* 30, 6672 (1936).

DI-(1-NAPHTHYLMETHYL) AMINE ACETATE

Synonym: α-Dinaphthomethylamine

$C_{22}H_{19}N$ Mol. Wt. 297.37

$C_{10}H_7—CH_2—NH—CH_2—C_{10}H_7$

Use: Determination and detection of nitric acid.

This compound is a pale yellow crystalline solid melting at 62° C.

Preparation: Dissolve 30 g. of α-naphthonitrile in 150 ml. of alcohol and 90 ml. of ethyl acetate. Add a quantity of nickel catalyst, and treat with hydrogen with shaking. Hydrogenation is complete in about 20 hours. Distill the mixture with steam until no more oil comes over, and extract the residue in the flask with ether in an extraction apparatus. Dry the ether solution and saturate with hydrogen chloride gas. The amine hydrochloride is precipitated as a pale yellow powder. Purify by recrystallizing from hot water.

To prepare the free base, shake the hydrochloride with dilute sodium hydroxide and ether. When the hydrochloride has passed into solution, evaporate the ether solution, finally in a vacuum to the complete removal of the ether. Recrystallize the residue several times from hot benzine, and convert to the acetate with acetic acid.

Determination of nitric acid. Di-(1-naphthylmethyl) amine acetate has been proposed by Rupe and Becherer[2] as a sensitive reagent for nitric acid. This reagent has been recommended as a more efficient precipitant for nitrate than nitron. A 10 per cent solution of the reagent in 50 per cent acetic acid is satisfactory for this purpose. The precipitate should be formed in 200 ml. of a boiling solution containing 2-10 ml. of 10 per cent sulfuric acid, and nitric acid equivalent to 0.1 g. of potassium nitrate. Phosphoric and sulfuric acids do not interfere, but other mineral acids should be absent. Nitrous acid forms with the reagent an insoluble nitrosoamine, and perchloric acid also forms an insoluble salt. Consequently these two acids must be absent in determining nitrate.

Konek[3] has used di-(1-naphthylmethyl) amine acetate to determine nitrates in fertilizer. His procedure is as follows:

Procedure. Digest 10 g. of the material to be analyzed with 1 liter of water. Filter and dilute 0.1 of the filtrate to 1 liter (this solution contains 1 g. of the fertilizer per liter). Dilute 10, 20, or 50 ml. of this last solution to 100 ml., and add 1-2 ml. of dilute sulfuric acid. Heat to 80-90° C., and add 2-5 ml. of 10 per cent solution of the reagent in 50 per cent acetic acid, cool, and allow to stand overnight. Filter, wash, dry, and weigh. One mg. of the precipitate is equivalent to 0.284 mg. of KNO_3.

The results obtained using this method are excellent.

Gutzeit[4] has used the reaction between nitric acid and the di-(1-naphthylmethyl) amine acetate as the basis for a test for nitrate.

1. H. Rupe and F. Becherer, *Helv. Chim. Acta.* **6**, 880 (1923).
2. H. Rupe and F. Becherer, *Helv. Chim. Acta.* **6**, 674-6 (1923); *C.A.* **17**, 3465 (1923).
3. F. Konek, *Z. anal. Chem.* **97**, 416-18 (1934); *C.A.* **28**, 5779 (1934).
4. G. Gutzeit, *Helv. Chim. Acta.* **12**, 713, 829 (1929).

DIPHENYLAMINE

$C_{12}H_{11}N$ Mol. Wt. 169.22 Beil. Ref. XII, 174(163)

$C_6H_5—NH—C_6H_5$

Uses: Detection of cerium, chlorine, chromium, manganese, nitrate, nitrite, oxidizing agents, oxygen, phosgene, vanadium and zinc.

Determination of nitrate, nitrite and vanadium.

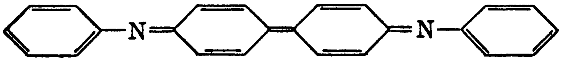
Diphenylamine is a colorless or white crystalline solid which melts at 53-54° C. and boils at 302° C. It becomes discolored on exposure to light. It is insoluble in water, but 1 g. of the solid dissolves in 2.2 ml. of alcohol and 4.5 ml. of propyl alcohol. It dissolves readily in benzene, ether, carbon disulfide and glacial acetic acid.

Preparation: Mix 10 g. of acetanilide, 5 g. of dry potassium carbonate and 20 g. of bromobenzene with a little cuprous iodide in nitrobenzene solution and reflux 15 hours. Distill the dark brown liquid until no more nitrobenzene passes over. The brown, oily residue in the flask consists of the acetyl derivative of diphenylamine. Dissolve in ether, filter, and dry over calcium chloride. Remove the ether on a water bath, and recrystallize the residue from alcohol. Dissolve the crystals in 30 ml. of alcohol, and hydrolyze by boiling with 30 ml. of concentrated hydrochloric acid for 2-3 hours. Distill with steam. The yellow oil which passes over solidifies in the condenser.[118]

Diphenylamine may also be prepared from aniline and aniline hydrochloride by the following procedure:

Procedure. Heat 93 g. of aniline and 93 g. of aniline hydrochloride for 20 hours at 230° C. in an autoclave. The pressure reaches 6 atmospheres. No iron should be in contact with the reaction products. After 2 hours heating, cautiously blow off steam through a valve. Repeat this operation three times during the hour. After 20 hours, mix the reaction product with 1 liter of water and heat to 80° C. Add about 70 ml. of concentrated hydrochloric acid until the mixture is just acid to Congo red. Allow to cool. After several hours pour off the supernatant liquid, and melt the crude diphenylamine under a little water. Extract any unchanged aniline with a little hydrochloric acid, and wash with dilute sodium carbonate. Purify the diphenylamine by distilling with superheated steam. The temperature of the oil bath in which the mixture is heated is 250° C. and that of the steam, 300° C. Diphenylamine is obtained as a colorless liquid which solidifies to a pale yellow solid.[119]

Detection of nitrite and nitrate. Diphenylamine is oxidized by nitric acid and other oxidizing agents to form a deep blue compound, which is the quinoid salt of *N,N'*-diphenylbenzidine:



This compound is formed by the oxidation and coupling of two diphenylamine molecules.[1,2] This reaction was first observed by Hoffman [8] and Merz and Weith,[4] and was later used by Kopp [8] and others [5,9,10] for the detection and determination of nitrites and nitrates in sulfuric acid. Böttger [7] proposed using Kopp's reaction for the detection of nitrites and nitrates in water.

Kehrmann and Micewitz [6] have studied the oxidation of diphenylamine, and have concluded that the reaction takes place in three steps: diphenylamine is first converted to tetraphenylhydrazine, which in turn rearranges to form diphenylbenzidine, and the latter is then oxidized to the quinoid salt:

(a) $2C_6H_5—NH—C_6H_5 + (O) \rightarrow (C_6H_5)_2{=}N—N{=}(C_6H_5)_2 + H_2O$

(b) $(C_6H_5)_2{=}N—N{=}(C_6H_5)_2 \rightarrow C_6H_5—NH—C_6H_4—C_6H_4—NH—C_6H_5$

(c) $C_6H_5—NH—C_6H_4—C_6H_4—NH—C_6H_5 + (O) \rightarrow$
$C_6H_5—N{=}C_6H_4{=}C_6H_4{=}N—C_6H_5 + H_2O$

The reagent used by Kopp[8] is prepared as follows:

Reagent. Dissolve 0.1 g. of diphenylamine in 5 ml. of concentrated sulfuric acid and about 5 ml. of water, and then dilute to 1 liter with concentrated sulfuric acid.

Procedure. A blue color is obtained when this reagent is added to an equal volume of a solution of a nitrite or nitrate.

Cimmino[11,12] suggests modifying the reagent used by Kopp by dissolving the diphenylamine in sulfuric acid containing 5-10 per cent hydrochloric acid. Withers and Ray[13-15] suggest the following reagent:

Reagent. Dissolve 0.7 g. of diphenylamine in 60 ml. of concentrated sulfuric acid and 28.8 ml. of water, and then add 11.3 ml. of hydrochloric acid (sp. gr. 1.19) after cooling.

Procedure. Add 1 drop of the reagent to 1 ml. of the solution to be tested, and float the mixture on concentrated sulfuric acid. Heat to 40° C. on a water-bath for 15-20 minutes. If nitrite or nitrate is present, a blue color appears. One part of nitric acid in 35,000,000 parts of solution and 1 part of nitrous acid in 25,000,000 parts of solution are said to be detectable by this method.

By heating the mixture 1 hour, the sensitivity is increased to 1 part of nitric acid in 44,000,000 and 1 part of nitrous acid in 32,000,000.

Allen[16,17] has used a method similar to that of Withers and Ray except that the test is made at room temperature instead of 40° C. The sensitivity of this procedure is said to be 1 part of nitrogen in 25,000,000 parts of solution.

Lunge[18] recommends the following procedure:

Reagent. Dissolve 0.5 g. of diphenylamine in 100 ml. of pure concentrated sulfuric acid diluted with 20 ml. of water.

Procedure. Place a few ml. of the diphenylamine solution in a test tube and carefully overlay with the solution to be tested for nitric acid. If the latter is present, a beautiful blue color is formed at the zone of contact of the two liquids.

This reaction is very sensitive but is also caused by nitrous, chloric and selenic acids, ferric chloride and many other oxidizing agents. The color is even obtained sometimes in the presence of fuming sulfuric acid.

If ferric and selenic salts are absent, this reaction may be used for detecting small quantities of the nitrogen acids in sulfuric acid.

Procedure. Pour the concentrated sulfuric acid to be tested into a test tube and cover with the diphenylamine solution. A blue color indicates the presence of nitrites and nitrates.

Sefton[19] has studied the use of diphenylamine for the detection of nitrates in battery acid, but has found the method unreliable. Przhevalskii and coworkers[20] have also used diphenylamine for the detection of nitric acid in sulfuric acid. Ivanov[21] has used a similar procedure for detecting nitric acid in sulfuric anhydride.

Thomann[22] has used diphenylamine for the detection of nitric acid in distilled water (*aqua distillatae*). Ghigliotto[23] has found that pieces of animal tissue which have been in contact with nitric acid produce a blue coloration when agitated with a solution of diphenylamine in sulfuric acid.

The diphenylamine reaction for nitrates may also be carried out as a spot test:

Reagent. Add a few crystals of diphenylamine to a little concentrated sulfuric acid and add sufficient water to cause complete solution. Mix with concentrated sulfuric acid so that 10 ml. of the solution contains about 1 mg. of diphenylamine.

Procedure.[1] Place 0.5 ml. of the diphenylamine solution on a spot plate, and to the middle of this solution add a drop of the material to be tested. A blue ring forms at the zone of contact between the two liquids if nitrate is present.

Alvarez[24,26,27] modified the diphenylamine reaction with nitrate by adding resorcinol to the solution of diphenylamine in sulfuric acid. This reaction is said to give a more permanent and distinctive test.

Reagent. Dissolve 0.1 g. of diphenylamine and 0.1 g. of resublimed resorcinol in 10 ml. of concentrated sulfuric acid.

Procedure. Place 1.0 mg. of the salt to be analyzed in a small flat-bottomed crucible and add 5-6 drops of the reagent. A stable yellowish-green color forms with nitrate. A blue color forms on diluting and blowing over the surface of the liquid. The addition of alcohol changes the color to orange.

An intense bluish-green color forms with nitrite, and upon shaking the crucible, the edge of the stain appears red. The liquid becomes red upon the addition of alcohol.

Tillmans[28-31] has reported that in testing for nitrate with diphenylamine, the presence of chlorides is essential. Tillmans and Sutthoff[32,33] claim that the methods of analysis previously applied to the detection and determination of nitrite and nitrate in water give irregular results, and this they believe is due in part to the lack of sufficient chloride. By adding sodium chloride as a reagent to the reaction mixture, the degree of accuracy uniformly obtainable is increased to 0.1 mg. of nitric acid per liter. The test is carried out as follows:

Reagent. Dissolve 0.085 g. of diphenylamine in 190 ml. of 1:3 sulfuric acid with the aid of some concentrated sulfuric acid, and then dilute to 500 ml. with concentrated sulfuric acid.

Procedure. Mix 100 ml. of the water to be tested with 2 ml. of a saturated sodium chloride solution and to 1 ml. of this mixture add 4 ml. of the reagent. A blue color forms if nitrate is present.

DeJong [34,35] has studied the method of Tillmans and Sutthoff [32,33] and claims that the more concentrated the reagent solution, the less sensitive the reaction. Hahn and Jaeger [36] have also studied the method of Tillmans and Sutthoff and reiterate the claim that the presence of chloride is essential. They suggest the use of a drop of hydrochloric acid. Hahn and Baumgarten [37] report that the diphenylamine test in the presence of chlorides is sensitive to 0.0001 mg. of nitric acid per ml.

Krauer [38,39] has found that on long standing a solution of diphenylamine in sulfuric acid may give a blue color, due perhaps to absorption of oxides of nitrogen from the air of the laboratory. He suggests that this difficulty may be eliminated by using solid crystals of diphenylamine for the detection of nitric acid in sulfuric acid. In this way as little as 0.00021 per cent of nitric acid in sulfuric acid is detected. Dilution with water intensifies ths color. Hahn [40,41] used this principle in preparing a dry reagent for the detection of nitrate. The test is carried out by mixing one part of solid diphenylamine with twenty parts of sodium chloride and adding to 20 mg. of this mixture, one ml. of water and two ml. of sulfuric acid.

Harvey [42] used the diphenylamine test for the detection of nitrate in plant tissue, and suggests using a reagent prepared as follows:

Reagent. Mix 0.05 g. of diphenylamine with 7.5 ml. of 95-96 per cent sulfuric acid and 2.5 ml. of 10 per cent aqueous potassium chloride solution.

Procedure. The test is carried out by applying the reagent directly to the tissue on a glass plate or a microscope slide.

The diphenylamine reaction for nitrate is limited in application due to the fact that many oxidizing agents, such as nitrous, chloric, perchloric, bromic, iodic, chromic, dichromic, molybdic, vanadic and hydroferrocyanic acids, hydrogen peroxide, sodium peroxide, barium peroxide, manganese dioxide, lead dioxide and ferric salts give similar blue colorations.[43-54]

Haun [53,54] has emphasized the necessity of using iron-free sulfuric acid in the nitrate test with diphenylamine. Sulfuric acid may be heated to reduce any trace of ferric to ferrous iron, since ferrous salts do not give a blue coloration with diphenylamine.

A blue color does not appear with nitric acid at ordinary temperatures if hydrochloric acid is used. The color, however, does appear with nitrites in a hydrochloric acid solution, and this makes possible the detection of nitrite and nitrate in the same solution. Nitrite is first detected with diphenylamine in the presence of hydrochloric acid, and the test for nitrate is then carried out by the usual procedure.[45,46]

Caron [55,58] has studied the diphenylamine reaction as applied to the detection of nitrates in wine or milk, and reports that three factors affect the efficiency of the test:

(a) The proportion of the reagent used has a marked effect on the sensitivity of the reaction, which is said to be more sensitive with smaller quantities of the reagent.

(b) The reaction depends upon the concentration of sulfuric acid used. Beyond a dilution of 30 ml. of water to 100 ml. of sulfuric acid the color formed diminishes.

(c) Heat increases the delicacy of the test.

Harvey [42] has also studied the factors controlling the production and intensity of color in the reaction between diphenylamine and nitric acid. He reports that (a) the concentration of sulfuric acid; (b) temperature of the reaction mixture; (c) time; and (d) order of mixing the reagents are important in color formation. Harvey [42] reports that three distinctive colors are observed in the diphenylamine-nitric acid reaction. These are: purple, blue, and green to yellowish-green. These depend upon the concentration of the sulfuric acid in the reaction mixture.

The difference in color appears to be due to the difference in oxidation and hydration of the diphenylamine molecule. Relationship of sulfuric acid concentration to color production is shown in Table 42.

TABLE 42.

Sulfuric Acid Concentration Per Cent	Color
87-97	Purple
83-87	Almost colorless
46-83	Blue
42-46	Slight blue-green, yellow or colorless
20-41	Green to yellowish-green

The maximum blue color is developed in a solution containing 72 per cent sulfuric acid. Temperature variations ranging from 20-50° C. appear to have slight effect except for the time required for color development. Investigations by Weinhagen [59] have confirmed the work of Harvey.

Barannikov [60] has emphasized that the blue color with diphenylamine appears even in the absence of nitrite and nitrate if active oxygen, produced in some way, is present. For example, when a solution of diphenylamine in concentrated sulfuric acid is electrolyzed, a blue color may be observed at the anode due to the oxygen formed.

Consequently, reactions in which oxygen is liberated must be avoided to prevent interference with the nitrate or nitrite test.

One of the principle uses of diphenylamine has been for the detection of nitrate in milk. This procedure may be used as a means of detecting added water.[28-31,55-58,61-63,67,112]

Reagent. Mix 0.085 g. of diphenylamine with 190 ml. of 1:3 sulfuric acid and add a little concentrated sulfuric acid. When the reagent is dissolved, dilute with concentrated sulfuric acid almost to 500 ml. Allow the mixture to cool, and then dilute to the mark with concentrated sulfuric acid.

Procedure. Treat the milk with calcium chloride, boil, and separate the serum. Shake 20 ml. of the serum with 5 ml. of lime water and about 25 ml. of pure ether to remove traces of fats and proteins.

Mix 2 ml. of the reagent in a test tube with 0.5 ml. of purified serum and allow to cool. Allow to stand for 1 hour and observe the color. If nitrate is present a blue color appears, but the color is yellow or pink if nitrate is absent.

Tillmans and Sutthoff [32,33] have used the diphenylamine test for the detection of nitrite.

Reagent. Dilute 500 ml. of the above nitrate reagent with 200 ml. of water.

Procedure. Mix 5 ml. of the reagent with 5 ml. of the solution to be tested. A blue color develops in the presence of nitrite and attains its maximum intensity in about 10 minutes. In this way, 0.1 mg. of nitrous acid can be detected in 1 liter of solution.

Hinrichs [45,46] has proposed a procedure for the detection of both nitrite and nitrate in the same solution. Karaoglanov [66] has used a procedure for detecting nitrite in the presence of nitrate and chlorate. The material to be tested is dissolved in 2 N acetic acid and volatile nitrous acid is removed by bubbling hydrogen through the solution. The gas is then passed over a drop of a solution of diphenylamine in sulfuric acid. If the liquid contains nitrite the reagent is colored blue.

There is no reliable test for traces of nitric acid in the presence of large quantities of nitrous acid in an aqueous solution. Many methods have been proposed which depend upon the destruction of nitrous acid by treatment with a primary amine, but these yield only approximate results. In order to destroy nitrites, it is necessary to add an acid to form free nitrous acid, and this always causes the oxidation of a part of the nitrous acid to nitric acid. For this reason, nitric acid will always be detected even when not originally present.

Soltsien [70,71] states that nitrous acid does not give a reaction with diphenylamine. According to Elsdon and Sutcliffe,[67] however, nitrous acid gives the test, and causes a deeper color when present in equivalent strength than does nitric acid, and in a shorter time.

Large quantities of nitric acid may be detected when in the presence of nitrous acid by a method proposed by Piccini.[72] In this procedure a concentrated solution containing both nitrite and nitrate is treated with a concentrated solution of urea, and is then carefully covered with a dilute solution of sulfuric acid. When the gases caused by the following reaction

$$CO(NH_2)_2 + 2HNO_2 \rightarrow CO_2 + 3H_2O + 2N_2$$

are no longer evolved, the solution is tested for nitric acid by means of diphenylamine. This reaction, however, does not take place quickly enough to prevent the formation of traces of nitric acid. If the diphenylamine reaction gives a very intense coloration after the destruction of nitrous acid with urea, the presence of nitric acid in the original sample is established; but if only a trace of nitric acid is indicated by the diphenylamine reacton, it is probably due to the formation of nitric acid during the reaction with urea.

Determination of nitrite and nitrate. The blue color formed in the reaction between diphenylamine and nitric acid is used for the colorimetric determination of small quantities of nitrates.[5,8,64,65,73-76,79,80] Since diphenylbenzidine is produced as an intermediate compound in the oxidation of diphenylamine to the blue quinoid salt, the former may also be used for the estimation of nitrates. A study of the two reagents indicates that diphenylbenzidine gives twice the color intensity produced by diphenylamine with the same quantity of nitrate.[77-80] The color produced with diphenylbenzidine is a violet-blue rather than a clear blue color, and is not as stable as the color produced with diphenylamine. For this reason diphenylamine appears to be the more practical reagent, but diphenylbenzidine should be used for determining smaller quantities of nitrate.

The conditions used in developing the color in the reaction between diphenylamine and nitric acid must be carefully controlled, since the color increases with increasing quantities of sulfuric acid and chloride, as well as of nitrate.[81] Change in temperature also changes the sensitivity of the reaction. The test is more sensitive after the temperature is raised, but the resulting color is not so permanent.[77] According to Smith [79,80] the stability and intensity of coloration are at a maximum at ordinary temperatures.

According to Riehm,[77,78] the test is more sensitive and the color produced is more bluish-violet and more permanent if the sulfuric acid and nitric acid content are increased and the excess of diphenylamine is made smaller. If an excess of diphenylamine is present, the color becomes bluer, and if a large excess is used a bluish-gray color appears.

According to Smith [79,80] the color obtained with diphenylamine in the determination of nitric acid according to Tillmans [32,33] decreases in intensity when the tube containing the mixture is shaken. He suggests as a probable explanation the formation of a volatile compound due to the oxidation of diphenylamine through the influence of hydrochloric acid. Riehm [77,78] states, however, that shaking produces no appreciable error.

Because of the influence of so many factors upon color development, a number of different reagents have been recommended. For example, Riehm [77,78] prepared a reagent containing 0.017 g. of diphenylamine, 33 ml. of water, and sufficient concentrated sulfuric acid to make 100 ml. of solution. This solution is known as a 33/17 reagent. The 33 refers to the number of ml. of water and the 17 the number of mg. of diphenylamine which are mixed with concentrated sulfuric acid to make 100 ml. of solution. Riehm recommends a 36/17 reagent when only a few determinations are to be made, and a 50/5 reagent when many determinations are to be carried out. A 38/5 reagent, however, gives the most permanent color scale, and is therefore the one most strongly recommended.

Smith [79,80] has also recommended a series of reagents for the nitrate determination. For concentrations of nitric acid ranging from 0.1 to 3.0 mg. N_2O_5 per liter, a reagent consisting of 0.04 g. of diphenylamine, 39 ml. of water and 68 ml. of concentrated sulfuric acid should be used. For water containing 1 to 25 mg. N_2O_5 per liter, a reagent consisting of 0.08 g. of diphenylamine, 20.5 ml. of water and 84 ml. of sulfuric acid is recommended. The procedure recommended by Smith is as follows:

Procedure. Place 4 ml. of the reagent in a test tube, and add with a pipet 1 ml. of the solution to be analyzed, which should contain 0.1 mg. of chloride per liter of solution. Mix well, cool with water, allow to stand about 1 hour, and then compare with standards similarly prepared.

Pfeilsticker [82] recommends the following procedure for determining nitrate with diphenylamine:

Reagents. *Sulfuric acid:* Add 2 g. of ammonium chloride to 1 liter of concentrated sulfuric acid and heat 1 hour at 180° C.

Diphenylamine solution. 90/100 *solution:* Add 100 mg. of diphenylamine to 900 ml. of water and slowly add 1 liter of the sulfuric acid reagent with cooling. Place 6 g. of ammonium chloride in a bottle and add 1 liter of the above solution.

80/100 *solution:* Prepare as described above, except that 800 ml. of water is used.

60/100 *solution:* Prepare as described above except that 50 mg. of diphenylamine and 600 ml. of water are used, and only 3 g. of ammonium chloride is placed in the storage bottle.

Standard nitrate solution: Dissolve 0.7216 g. of pure potassium nitrate in water and dilute to 1 liter. Preserve with a little toluene. This solution contains 100 mg. of nitrogen per liter, and is diluted as needed to prepare standards of suitable nitrate content.

Procedure. Carry out a preliminary determination with reagents 90/100 and 80/100 as follows: Place 1 drop of the solution to be analyzed on a spot plate and add 10 drops of either reagent. If a medium or dark blue color appears within 3 minutes, dilute the sample at least 100-fold. If only a pale blue color develops in less than 5 minutes, dilute 10-fold. If a pale blue color develops within 5-10 minutes dilute with an equal volume of water. If a blue color develops very rapidly, nitrites are probably present. If sufficient nitrite is present to interfere with the determination, add to 10 ml. of the solution, 20 mg. of urea and 1 drop of concentrated sulfuric acid and allow to stand over night.

Having diluted the sample properly according to the preliminary determination, proceed with the final determination as follows:

90/100 *reagent:* Place 0.5 ml. of the properly diluted sample in a small tube and add 5 ml. of the reagent slowly so that the temperature does not rise. The addition of the reagent, however, should not require more than 20 minutes. Stir or shake until the solution is perfectly clear. Place 0.5 ml. of standard solutions containing 1.0, 2.0 and 5.0 mg. of nitrogen per liter in similar tubes and treat in the same manner. Allow to stand for 1-3 hours and compare the color of the unknown solution with that of the closest standard. The 80/100 reagent is used in the same way.

60/100 *reagent:* This reagent is used as described above, except that the addition of the reagent to the solution and the mixing must not require more than 10 minutes. The standards used should contain 0.1, 0.2 and 0.5 mg. of nitrogen per liter.

To determine nitrate in the presence of nitrite, the nitrite is determined separately and subtracted from the total as estimated by the diphenylamine reaction. The error in this procedure is only about 2 per cent.[83,84]

Morgan [85] has proposed a spot plate method for the approximate estimation of nitrate which can be used in field work or under circumstances where more accurate determinations are not possible. Good results have been reported by this method in the analysis of soil extracts and plant tissue.

Reagents. *Diphenylamine reagent:* Dissolve 50 mg. of diphenylamine in 25 ml. of concentrated sulfuric acid. Do not use after 2 or 3 days.

Standard nitrate solution: Dissolve 0.7216 g. of pure potassium nitrate in sufficient distilled water to make 1 liter of solution. This solution contains 100 p.p.m. of nitrate nitrogen.

Procedure. Prepare a series of standards containing 1, 2, 3, 5, 7, 10, 15 and 20 p.p.m. of nitrate nitrogen by diluting the standard with distilled water.

Place a drop of each of the standard solutions and 1 drop of the sample on a spot plate, and add to each of the drops 4 drops of the diphenylamine solution. Mix well and allow to stand for 2 minutes. A blank with distilled water should give no color. Variations in color cannot be observed readily if the concentration of nitrogen is above 25 p.p.m. If the concentration of the unknown is greater than 25 p.p.m., dilute with water.

Tassilly and Savoire [86,87] used diphenylamine for the determination of 0.1-5 mg. of N_2O_3 and nitrates.

Tillmans and co-workers [28-31,88-91] used diphenylamine for the determination of nitrate in milk. The method used is essentially that described in the section on detection of nitrates in milk (page 360).

Elsdon and Sutcliffe [67] report that best results are obtained by preparing the milk serum according to the method of Tillmans and Sutthoff.[68,69]

Tillmans and Sutthoff [32,33] used diphenylamine for the determination of nitrite and nitrate in water. The method as originally employed gave irregular results, but this has been remedied by the addition of sodium chloride to the reaction mixture. Alten and Weiland [92] report that this method is fairly accurate for 1-2.5 p.p.m. of nitrate, and is not affected adversely by the presence of chlorides.

Riehm [77,78] has used diphenylamine for the determination of nitric acid in soil. Caron [93,94] has also used this reagent for the determination of nitric acid in urine, but results are only approximate. The method, however, is easy and rapid and requires only a few ml. of sample. Tillmans and Splittgerber [95] used diphenylamine for the determination of nitric acid in natural fruit juices.

Diphenylamine has also been used for the determination of the oxides of nitrogen in air.[96,117] The following method has been described by Heim and Herbert.[96]

Procedure. Aspirate a definite volume (approximately 1 liter) of air through a 10-ml. absorption tube filled with 5 per cent potassium hydroxide, and dilute the solution to 500 ml. Mix well and place 1 ml. of this solution in a test tube. Then add 5 ml. of a reagent prepared by dissolving 0.2 g. of diphenylamine in 1 liter of concentrated sulfuric acid, and compare the resulting color with that produced by a standard solution of potassium nitrate.

Oxidizing gases and organic matter must be absent.

Detection of oxidizing agents. A blue color similar to that formed by nitrate and nitrite is produced in a solution of diphenylamine sulfate in the presence of dichromate, hypochlorite, permanganate, perchlorate, manganese dioxide and hydrogen peroxide. In the absence of hydrochloric acid, potassium dichromate produces a green color and potassium permanganate a yellow color with the reagent.[97] In addition to the above mentioned oxidizing agents, many others such as perchlorate, bromate, iodate, molybdate, vanadate, ferricyanide, chromate, sodium peroxide, barium peroxide, lead dioxide, periodate and ferric salts also give a blue color with diphenylamine.[49-54] Ekkert [43,44] recommends the following procedure for detecting oxidizing agents.

Procedure. To a few drops of a solution containing 0.01 g. of the oxidizing agent, add 4-5 ml. of 33 per cent hydrochloric acid and then 1-2 drops of a solution of 0.5 g. of diphenylamine in 100 g. of acetic acid. Dilute with water and observe the blue color which forms if oxidizing agents are present.

Lang [98] has used the reaction of diphenylamine with chromium, manganese, cerium and vanadium for the detection of these metals. The reaction detects 1γ of chromium, 10γ of manganese, 30γ of cerium and 2γ of vanadium.

Hager [99] and LeRoy [100] used diphenylamine for the detection of chlorine with which it produces a blue color. Schmalfuss and Werner [101] used a similar reagent to detect oxygen. When a drop of 1 per cent solution of diphenylamine is placed in 18 N sulfuric acid and treated with nitric oxide, it becomes blue in the presence of oxygen. This reaction detects as little as 0.002 ml. of oxygen in 200 ml. of a gaseous mixture.

Detection and determination of vanadium. Vanadium is detected by the blue color which forms in the reaction between vanadates and diphenylamine. Meaurio [102-104] has used this reaction for the detection and determination of vanadium in water:

Reagent. Add 0.2 g. of diphenylamine to 100 ml. of water and warm on a water-bath. Cool and filter. This reagent is not affected by prolonged contact with air or exposure to light.

Procedure. To 3-4 ml. of the water to be tested, add 1 ml. of concentrated hydrochloric acid and 1 ml. of the reagent. Shake the mixture but do not warm. A violet coloration is produced if vanadium is present. The intensity and rate of appearance of the coloration depends upon the quantity of vanadium present. By this test 0.005 mg. of NH_4VO_3 in 2 ml. of water can be detected.

This reaction is made quantitative by comparing the color of the unknown solution with that of standards containing known quantities of ammonium vanadate. The optimum temperature is 50° C. and the mixture should stand for 10 minutes for maximum color development.

Nitrate in quantities usually found in water does not interfere with this test, but in the presence of an excess of free nitric acid, proceed as follows:

Procedure. Add 30 per cent sodium hydroxide solution carefully to the unknown solution until the mixture is alkaline to phenolphthalein, and then shake with 1 ml. of a saturated alcoholic solution of oxalic acid. Add 1 ml. of concentrated hydrochloric acid and 1 ml. of diphenylamine solution. A violet color forms within 2 minutes if vanadium is present.

Ferric salts in quantities usually found in water, do not affect this reaction, but when an excess of iron is present, proceed as follows:

Procedure. Treat the solution with hydrochloric acid until a yellow color appears and then with phosphoric acid, ammonium phosphate or ammonium fluoride until the solution is decolorized. Add 1 ml. of hydrochloric acid and 1 ml. of the reagent, and again decolorize the liquid if necessary. A violet color appears within 1 minute if vanadium is present.

The diphenylamine method for detecting vanadium may also be used in the presence of titanium.

If there is any question as to whether the violet color with diphenylamine is caused by vanadium or nitric acid, shake the mixture with 1 ml. of chloroform; the chloroform layer becomes yellow when the reaction is caused by nitric acid, but remains colorless if the reaction is due to vanadic acid.

Moser and Brandl[105] have studied the various methods proposed for the detection of vanadium, and report that diphenylamine is less satisfactory than the hydrogen peroxide, phosphotungstic acid, thiocyanate and tannin methods.

Detection of manganese. Fresenius[107] has recommended the use of diphenylamine for the detection of manganese as the permanganate ion. Wenger and co-workers,[106] who have studied the many reactions proposed for the detection of manganese, report that this method gives satisfactory results. By means of the blue color which forms, 0.01γ of manganese in 0.05 ml. of solution can be detected, although oxidizing agents interfere. Dubsky and Langer[108] have also reviewed the use of diphenylamine for the detection of manganese.

Detection of zinc. In the systematic analysis of the iron and aluminum group in qualitative analysis, a solution is obtained which contains zinc and possibly chromium. Cone and Cady[109] have proposed a method for testing this solution for zinc.[113,114]

Procedure. Acidify the solution with acetic acid, and add 5 drops of a 1 per cent solution of diphenylamine in glacial acetic acid and 5 ml. of a 0.5 per cent solution of potassium ferrocyanide. The immediate appearance of a dark brown, green, or dark purple turbidity indicates the presence of zinc. The quantity of zinc can be estimated by the depth of color of the solution.

Detection of chromium. Knop [110] has stated that in the absence of iron salts, no coloration is produced by dichromates in a dilute solution of diphenylamine sulfate. Cone and Cady,[109] however, report that this is true only when the concentration of the dichromate is less than 0.05 mg. per ml. A blue color is produced immediately if the concentration of the dichromate is greater than 0.05 mg. per ml. By using diphenylamine acetate instead of diphenylamine sulfate, however, no color is produced unless the chromium concentration is greater than 10 mg. of potassium dichromate per ml. of solution.

Leibov [115] has studied the use of diphenylamine for the colorimetric determination of chromium, but reports that it is unsatisfactory.

Detection of phosgene. Diphenylamine is used for the detection of phosgene.[111]

Substituted diphenylamines. Yoe [116] has studied the analytical properties of a number of substituted diphenylamines.

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DIPHENYLAMINE-2,2′-DICARBOXYLIC ACID

$C_{14}H_{11}O_4N$ Mol. Wt. 257.23 Beil. Ref. XIV, 354(545).

$$HO_2C—C_6H_4—NH—C_6H_4—CO_2H$$

Use: Detection of oxidizing agents.

Diphenylamine-2,2′-dicarboxylic acid is a yellow crystalline solid which melts at 296-297° C. with decomposition. It is insoluble in water, but is slightly soluble in alcohol, ether and chloroform.

Preparation: Diphenylamine-2,2′-dicarboxylic acid is prepared by heating the alkali salt of 2-chlorobenzoic acid and anthranilic acid in the presence of copper and with water in a closed tube at 115-120° C. It may also be prepared by boiling potassium chlorobenzoate with anthranilic acid and anhydrous sodium carbonate in the presence of copper in the smallest possible quantity of amyl alcohol.

Detection of oxidizing agents. Diphenylamine-2,2′-dicarboxylic acid is used instead of diphenylamine in reactions with oxidizing agents. It may be used as an oxidation-reduction indicator in strongly acid solutions, and is satisfactory in solutions which are 16-20 normal in sulfuric acid.

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DIPHENYLAMINESULFONIC ACID

$C_{12}H_{11}O_3NS$ Mol. Wt. 249.28 Beil. Ref. XIV, 699(721).

$C_6H_5—NH—C_6H_4—SO_3H$

Uses: Detection of oxidizing agents.

Determination of nitrates.

Diphenylaminesulfonic acid occurs as leaves which are easily soluble in water and alcohol. It is insoluble in ether.

Preparation: The reagent is usually prepared as the barium salt. Treat equimolecular quantities of diphenylamine and acetic anhydride with a few ml. of concentrated sulfuric acid and heat under reflux for 1 one hour. Remove the acetic acid by washing the product with cold water, and then recrystallize the acetyldiphenylamine two times from ether. Dry at 100° C.

Cool 200 g. of 20 per cent fuming sulfuric acid to 5° C., and add 100 g. of the powdered acetyldiphenylamine in small portions with constant stirring. Warm the mixture to 45° C. on a water bath for 2 hours with stirring. Pour the mixture into 250 ml. of water and boil 3 hours to hydrolyze the acetyl derivative, and then pour into a large volume of water. Filter off any unchanged diphenylamine, and neutralize the filtrate with barium carbonate. Filter off the barium sulfate. The barium diphenylaminesulfonate which is obtained from the filtrate is separated from barium acetate by fractional crystallization.[1,5]

Detection of oxidizing agents. Diphenylaminesulfonic acid has been employed primarily as an oxidation-reduction indicator, although it may be used to detect oxidizing substances,[2,3] and for the colorimetric determination of nitrates.[4] Kolthoff and Sarver[5] first suggested the use of this reagent as an oxidation-reduction indicator. The oxidation mechanism of this compound is the same as diphenylamine, although it is superior to the latter for the following reasons: (a) it is more soluble in water, (b) it exhibits a sharp color change, and (c) it may be used in the presence of tungstic acid. An aqueous solution of the barium salt is used.

Determination of nitrate. Kolthoff and Naponen[4] claim that sodium diphenylaminesulfonate is superior to diphenylamine or benzidine for the colorimetric determination of nitrate. The oxidation product formed in a strongly acid solution has a bluish-violet color, whereas diphenylamine yields an indigo-blue color. Using sodium diphenylamine sulfonate, 1-50 mg. of nitrate in 10 ml. of solution may be determined with an accuracy of 5 per cent.

Sodium diphenylamine sulfonate. Prepare a 0.006 M solution as follows: dissolve 0.512 g. of the barium salt of the reagent in about 125 ml. of water, and to this add 0.117 g. of anhydrous sodium sulfate dissolved in a little water. Filter off the barium sulfate, and dilute the filtrate to 250 ml. with water.

Procedure. Prepare a series of standards, each containing 10 g. of potassium chloride and 0.1, 0.2, 0.3, 0.4, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0 mg. of nitrate ion, respectively, per liter. To the aqueous solution of the nitrate to be analyzed, add potassium chloride to a concentration of 8-12 g. per liter. Now treat both standards and unknown as follows: to 10 ml. of the nitrate-potassium chloride solution add 10 ml. of sulfuric acid from a pipet. Immediately after adding the acid, immerse the flask in cold water and stir the contents thoroughly. Cool to room temperature and add 0.1 ml. of the 0.006 M sodium diphenylaminesulfonate solution. Mix thoroughly and compare in a colorimeter.

There is no exact proportionality between the intensity of color and the nitrate concentration; hence, the nitrate concentration must be calculated by the following empirical method: suppose the unknown was found to contain between 2 and 3 mg. of nitrate; then with the 3 mg. standard set at a reading of 20, the 2 mg. standard read 35 and the unknown 30. The concentration of the unknown then is equal to

$$2 + \frac{35 - 30}{35 - 20} = 2.33 \text{ mg. per liter}$$

Nitrite interferes with the determination and must be removed with ammonium chloride. Urea cannot be used, since an excess of this compound interferes with the color formation.

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DIPHENYLBENZIDINE

$C_{24}H_{20}N_2$ Mol. Wt. 336.42 Biel. Ref. XIII, 223(61).

$C_6H_5—NH—C_6H_4—C_6H_4—NH—C_6H_5$

Uses: Detection of nitrate, nitrite and zinc.

Determination of nitrate and nitrite.

Diphenylbenzidine is obtained as leaves by crystallizing from toluene. It melts at 244-245° C. This compound dissolves readily in boiling toluene and acetic acid, but dissolves only slightly in alcohol, acetone and benzene. The solution of diphenylbenzidine in cold, concentrated sulfuric acid is colorless, but on heating becomes a dirty reddish-violet. A solution of diphenylbenzidine in concentrated sulfuric acid is colored blue by nitrites and nitrates. The reagent dissolves in acetic acid to form a light yellow solution, but this is colored blue in the presence of dichromates and greenish-yellow with ferric chloride.

Preparation: Mix 1 liter of concentrated sulfuric acid, 2 liters of glacial acetic acid and 12 liters of water, and add slowly with stirring a solution of 50 g. of diphenylamine in 500 ml. of acetic acid. If any diphenylamine separates, redissolve by warming the mixture to a temperature not exceeding 50° C. To the resulting solution at 15-25° C., add slowly and with vigorous stirring a solution of 22 g. of potassium dichromate in 500 ml. of water. Allow to stand 5 minutes and reduce the excess dichromate with a solution of 10 g. of sodium bisulfite. Filter, and place the greenish-black product, while still moist, in a warm concentrated solution of sodium bisulfite. When the color is light brown, filter, wash with hot water, and dry thoroughly. Pulverize and extract the solid with 1250 ml. of boiling xylene. Again extract the residue with the same solvent. Pure diphenylbenzidine separates on cooling. Filter and wash the crystals with alcohol until the washings fail to give a white cloud on dilution with water. Dry at 110° C.[1,11,16]

Detection of nitrates and nitrites. Wieland [2,3] and Kehrmann and Micewitz [4] have studied the oxidation of diphenylamine, and have concluded that the reaction occurs in 3 stages: (a) the formation of tetraphenylhydrazine; (b) rearrangement to diphenylbenzidine; and (c) the oxidation of diphenylbenzidine to an imonium derivative (page 356). Since diphenylbenzidine appears to be formed as an intermediate product in the oxidation of diphenylamine, which is a sensitive reagent for nitrates, Letts and Rea [5] and Monnier-Williams [15] have concluded that diphenylbenzidine should be the more satisfactory reagent for the detection and determination of nitrates. This reagent utilizes more effectively the oxidizing action of the nitric acid. In the presence of an excess of diphenylamine, it is possible for the oxidation to terminate with the formation of diphenylbenzidine, and in this case no color will appear. This color reaction is not specific for nitric acid, but occurs also with other oxidizing agents, such as nitrite, chlorate, bromate, iodate, chromate, permanganate, vanadate, molybdate, peroxides and ferric salts. According to Smith,[6] diphenylbenzidine is about two times as sensitive as diphenylamine toward nitrates. The following procedure may be used for the detection of nitrates and nitrites.[5]

Procedure. Mix 0.5 ml. of solution to be tested with 1.3 ml. of pure sulfuric acid in a small porcelain crucible, and add 0.5 ml. of a solution prepared by dissolving 0.01 g. of diphenylbenzidine in 50 ml. of concentrated sulfuric acid. A blue color appears with either nitrate or nitrite.

Determination of nitrate. Small quantities of nitrate are determined colorimetrically by means of the blue color which is formed when a solution of diphenylbenzidine in concentrated sulfuric acid is allowed to react with a solution of a nitrate.[5-9] The intensity of the blue color depends upon temperature, time, and the proper proportion and order of adding the reagents. For this reason the colorimetric determination of nitrate requires strict attention to detail of procedure. According to Letts and Rea,[5] optimum conditions are obtained as follows:

Procedure. Use 0.5 ml. of the solution to be analyzed, 1.2 ml. of pure sulfuric acid, and 0.3 ml. of a solution prepared by dissolving 0.01 g. of diphenylbenzidine in 50 ml. of concentrated sulfuric acid. Stir the mixture with a glass rod, allow to stand for 10 minutes, and then observe the color. If the solution to be analyzed is too concentrated, dilute 0.1 ml. of the solution to 0.5 ml. with distilled water. Carry out the reaction and the color comparison in a 20 ml. porcelain crucible. Compare with standards similarly prepared containing from 0 to 1.0 part of nitrate nitrogen per 100,000 parts of solution.

Nitrite may be determined after conversion to nitrate by oxidation.

Stromberg[7] recommends the following procedure for the determination of nitrate and nitrite in biological specimens:

Reagent. Dissolve 50 mg. of diphenylbenzidine in 200 ml. of concentrated sulfuric acid. When the solid is completely dissolved, carefully add an equal volume of water and cool before using.

Procedure. Free the sample to be analyzed of proteins and chlorides and filter. Dilute the filtrate so that the concentration of nitrate and nitrite lies between 0.0002 and 0.0009 mg. of nitrogen per ml. Place 1 ml. of the diluted material in a test tube fitted with a glass stopper, and add 0.1 ml. of a solution of sodium chloride containing 12.5 mg. of the salt per ml. Then add 10 ml. of the diphenylbenzidine solution, and immediately add 10 ml. of concentrated sulfuric acid. Stopper the tube, mix by inverting the tube two times, and place the mixture in an ice bath for 20 minutes. Allow to come to room temperature, and after one and three-quarters hours compare in a colorimeter with a standard solution having a concentration of 0.0005 mg. nitrogen as nitrate per ml. The standard solution is prepared by dissolving 0.18043 g. of potassium nitrate in a liter of solution. One ml. of this solution contains 0.025 mg. of nitrogen per ml. The final standard is prepared by diluting 10 ml. of this solution to 500 ml. The color of the standard solution is considered as unity and corrected values for the quantities of nitrate and nitrite are obtained by reference to a previously prepared chart.

Atkins[9] has used diphenylbenzidine for the estimation of nitrates in sea water. The following procedure is used:

Procedure. Mix 2.5 ml. of water to be analyzed with 6 ml. of concentrated sulfuric acid and allow to cool. Treat the mixture with 1.5 ml. of a reagent prepared by dissolving 20 mg. of diphenylbenzidine in 100 ml. of concentrated sulfuric acid. Allow the mixture to stand for 24 hours and compare the color with a standard solution of a nitrate prepared in sea water.

The sulfuric acid used in this procedure must be free from nitrate. Nitrate-free sulfuric acid is prepared by heating concentrated sulfuric acid, or by adding a small amount of hydrogen sulfide. Ferric iron gives a test similar to that with nitrate, but the concentration of iron in sea water is too low to interfere with this determination.

Riehm [10] has reported that the reaction between nitrate and diphenylbenzidine gives a deeper color and a more violet shade when chlorides are present. Further, a rise in temperature makes the test more delicate. The permanence of the color appears to depend upon the ratio of the reagent to the nitrate content of the solution. The depth of color is nearly twice that obtained with diphenylamine, and the stability of the blue-violet color is much more sensitive to the presence of an excess of diphenylbenzidine.

Detection of zinc. Diphenylbenzidine may be used in place of diphenylamine with potassium ferricyanide for the detection of zinc. The test is carried out by substituting diphenylbenzidine for diphenylamine in the procedure described on page 366.[12,14]

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s-DIPHENYLGUANIDINE

Synonym: Melaniline

$C_{13}H_{13}N_3$ Mol. Wt. 211.26 Beil. Ref. XII, 369.

$(C_6H_5NH)_2{=}C{=}NH$

Use: Standard in acidimetry and alkalimetry.

This reagent is a white, crystalline solid. It melts at 148° C., and decomposes at about 170° C. It is only slightly soluble in water, but is soluble in alcohol, chloroform, hot benzene, or toluene. It is a strong base and dissolves in dilute mineral acids. It is a mono-acid base, having an equivalent weight of 211.26.

Preparation: Mix diphenylthiourea with an excess of strong potassium hydroxide, and add an equal volume of concentrated ammonia. Then add for each mole of diphenylthiourea a paste prepared by mixing 1.5 moles of litharge with water. Digest on a water bath until a few drops of the liquid shows no darkening when heated with a lead salt. Extract with dilute hydrochloric acid and precipitate with sodium hydroxide. Purify by crystallizing from alcohol.[1]

Standard in acidimetry and alkalimetry. Carlton [2] has proposed the use of *s*-diphenylguanidine as a reliable standard for titrations in acidimetry and alkalimetry. His work shows that results obtained using this reagent agree within 1 part per 1000 with results obtained by weighing silver chloride, and with those obtained using sodium carbonate. Chakmakjian [3] and Young [4] confirm Carlton's claims, but other investigators report unsatisfactory results. Kling and Lassieur [5] report the reagent unsatisfactory because it does not give a good end-point with methyl orange or with bromphenol blue. Thornton and Christ [6] also claim unsatisfactory results with this reagent. A comparison between the normality of a basic solution using *s*-diphenylguanidine with values obtained with constant-boiling hydrochloric acid shows that results are about 0.56 per cent too low. Results appear to be uncertain because of the difficulty in preparing the pure reagent from the commercial product. Recently Young [4] has suggested that a satisfactory standard may be obtained by recrystallizing the reagent. Results of the titration of an alcoholic solution of the base to pH 5.2 for a N acid, or of pH 5.6 for a 0.1 normal acid agree within the limits of experimental error with results obtained with sodium carbonate or borax.

The crystalline product may be stored in glass-stoppered bottles without alteration, but solutions of the reagent do not keep long because the base is saponified with the formation of urea.

The reaction between the base and hydrochloric acid is represented by the equation,

$$(C_6H_5{-}NH)_2{=}C{=}NH + HCl \rightarrow (C_6H_5{-}NH)_2{=}C{=}NH_2Cl.$$

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3. H. H. Chakmakjian, *J. Chem. Ed.* **8**, 2060-1 (1931); *C.A.* **25**, 5874 (1931).
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as-DIPHENYLHYDRAZINE

$C_{12}H_{12}N_2$ Mol. Wt. 184.23 Beil. Ref. XV, 122.

$$(C_6H_5)_2{=}N{-}NH_2$$

Use: Detection of selenium.

as-Diphenylhydrazine is obtained as yellow plates by crystallization from ligroin. It melts at 34.5° C., boils at 220° C./40 mm., and has a sp. gr. of 1.19. It is very slightly soluble in water, but is easily soluble in ether, alcohol, benzene, and chloroform.

Preparation: Dissolve 50 g. of diphenylnitrosoamine in 250 ml. of ethyl alcohol, and add 75 g. of zinc dust. Then with good cooling and continuous agitation, add glacial acetic acid slowly until heat is no longer generated, and until a filtered sample shows no bluish-green color on the addition of concentrated hydrochloric acid. Filter hot, and concentrate the filtrate to one-fourth its volume, and then dilute with an equal volume of water. Add a large excess of hydrochloric acid, while cooling and stirring. Upon cooling, a mixture of the hydrochlorides of diphenylhydrazine and diphenylamine separate. Dissolve the crude product in hot, very dilute hydrochloric acid, and remove the oily diphenylamine by filtration. Mix the filtrate with concentrated hydrochloric acid to precipitate diphenylhydrazine hydrochloride. Repeat the operation several times if necessary to secure a good separation. Finally, purify by recrystallizing from alcohol. The free base is obtained as a yellow oil by treating the hydrochloride with an excess of sodium hydroxide and extracting with ether.[1]

Microdetection of selenium. A sensitive test for selenium is based on the oxidation of *as*-diphenylhydrazine by means of selenium dioxide. This reaction is used for the detection of selenium, selenides, selenites and selenates.[2]

Procedure. Mix 4 drops of a 1 per cent solution of *as*-diphenylhydrazine in glacial acetic acid with 1 drop of 2 N hydrochloric acid and 1 drop of the solution to be tested. A red color appears immediately if selenious acid is present, unless the solution is very dilute. In this case the mixture should be heated and allowed to stand before comparison with a blank. As little as 0.001 per cent selenium can be detected in a sample containing selenium.

In the presence of oxidizing agents, it is necessary to evaporate the solution to dryness with hydrochloric acid and oxalic acid. Minerals are decomposed with hydrochloric acid and hydrogen peroxide.

1. E. Fischer, *Ann.* **190**, 175 (1878).
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DIPHENYLINE

Synonym: 2,4′-diphenyldiamine, o,p′-dianiline

$C_{12}H_{12}N_2$ Mol. Wt. 184.22 Beil. Ref. XIII, 211.

$$H_2N—C_6H_4—C_6H_4—NH_2$$

Use: Detection of tungsten.

Diphenyline is obtained as needle-like crystals from alcohol. The compound melts at 45° C., and boils at 363° C. It is very slightly soluble in water, but dissolves readily in alcohol and ether.

Preparation: Mix gradually a hot alcoholic solution containing 70 g. of azobenzene with a solution of 53 g. of tin dissolved in concentrated hydrochloric acid. Distill off the alcohol and mix the residue with sulfuric acid. In this way benzidine sulfate is precipitated, while diphenyline and aniline remain in the solution. Filter, make the filtrate alkaline, and extract the mixture with benzene.

Shake the benzene solution with hydrochloric acid, and evaporate the acid solution. Crystals of diphenyline are obtained.[1]

Detection of tungsten. Tungsten, as the tungstate, may be detected by its reaction with diphenyline.[2,3]

Procedure. Place 1 drop of the tungstate solution in a microtest tube and add 1 drop of diphenyline hydrochloride solution. A white turbidity or precipitate appears with as little as 6γ of tungsten at a limiting dilution of 1:8,500. Molybdenum and sulfates do not interfere.

1. G. W. Fischer, *Monatsh.* **6**, 547 (1885).
2. F. Feigl, *Rec. trav. chim.* **58**, 471-80 (1939); *C.A.* **33**, 5771 (1939).
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DIPROPYLAMINE

$C_6H_{15}N$ Mol. Wt. 101.19 **Beil. Ref. IV, 138.**

$$C_3H_7—NH—C_3H_7$$

Use: Precipitation of metals.

Dipropylamine is a colorless liquid. It has a strong odor of ammonia. It boils at 110° C., and has a sp. gr. of 0.738. It is freely soluble in water and alcohol.

Preparation: Dipropylamine is prepared by heating propyliodide with ammonia on a water-bath.[1]

Determination of magnesium. Dipropylamine like dimethylamine [2] may be used for the quantitative precipitation of magnesium hydroxide from solutions of magnesium salts.

Reactions with metals. Vincent [3,4] has used dipropylamine to precipitate those metals which form insoluble hydroxides, and has used this reaction for the detection of these metals. These reactions are not in any wise specific, however, and their value as analytical procedures is not great.

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2. G. Hemming, *Z. anorg. Chem.* **130**, 333 (1923); *C.A.* **18**, 799 (1924).
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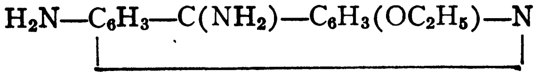
2-ETHOXY-6,9-DIAMINOACRIDINE HYDROCHLORIDE

Synonym: Rivanol

$C_{15}H_{15}ON_3$ Mol. Wt. 253.27



$$\underbrace{H_2N—C_6H_3—C(NH_2)—C_6H_3(OC_2H_5)—N}$$

Use: Determination of nitrite.

This compound is a light yellow crystalline solid. It dissolves in 260 parts water, 28 parts boiling water, and 200 parts alcohol.

Determination of nitrite. Rubel[1] has suggested the use of the antiseptic "Rivanol" as a satisfactory reagent for the colorimetric determination of nitrite.

Procedure. Add 0.5 ml. of a 0.1 per cent solution of the reagent and 0.5 ml. of hydrochloric acid ($d = 1.06$) to 10 ml. of the diluted solution to be analyzed. A yellow-green to orange or red color is obtained depending on the amount of nitrite present. This color is compared with standard solutions of sodium nitrite treated in a similar manner. The standards should contain 0.1-0.001 mg. of N_2O_3 as $NaNO_2$.

The color obtained in the above procedure changes to yellow on heating. It is stable about an hour in the light, after which a brown precipitate forms. It is stable for longer periods if kept in the dark. The reaction employing "rivanol" is more sensitive (0.001 mg /10 ml.) than *m*-phenylenediamine. It has about the same sensitivity as that of the Griess reaction, but the color is more stable than that obtained in the latter, and, unlike it, is unaffected by phenol and ammonium salts, and is only slightly suppressed by thymol. Amino acids, less than 10 per cent of sodium chloride, nitrates, glucose and lactic acid have no effect upon this reaction. Aldehydes weaken the color. Free iodine causes a greenish-blue color. Free ammonia interferes and must be neutralized.

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1. W. M. Rubel, *Z. Untersuch. Lebensm.* **60**, 588-92 (1930); *C.A.* **25**, 3928 (1931).

ETHYL AMINE

C_2H_7N Mol. Wt. 45.08 Beil. Ref. IV, 87.

$C_2H_5NH_2$

Use: Detection of hydrogen cyanide.

Determination of aluminum and beryllium.

Ethyl amine is a colorless, inflammable, light liquid. It has an ammoniacal odor, and is strongly alkaline in character. It boils at 19° C. and has a sp. gr. of 0.689. It is miscible with water, alcohol and ether. The compound must be kept in a tightly closed container and in a cold place.

Preparation: Add 1 mole of propionamide to 1 mole of bromine, and mix in the cold with a 10 per cent solution of potassium hydroxide until a yellow color appears. Then pour this solution carefully in a slow stream from a dropping funnel into a 30 per cent solution of potassium hydroxide containing 3 moles of potassium hydroxide, which has previously been heated to 60-70° C. The temperature should not rise above 70° C. Digest at this temperature until the solution is completely colorless (10-15 minutes). Distill, collect the distillate in hydrochloric acid. The hydrochloride may be obtained by evaporating this solution.[1]

Determination of aluminum. Kozu[2] used ethylamine to precipitate aluminum hydroxide from solutions of aluminum salts.

Procedure. Add ethylamine to a solution of potash alum containing a few drops of bromothymol blue indicator solution until the mixture turns green. Allow to stand for 30-50 minutes and heat on a water-bath. Aluminum hydroxide is precipitated completely and in compact form by this treatment.

The pH of the above solution is approximately 7.9. Aluminum hydroxide dissolves in an excess of ethylamine when the pH of the solution is above 10.5, although it is reprecipitated when carbon dioxide is passed into this mixture.

Determination of beryllium. Beryllium hydroxide may be precipitated quantitatively by means of ethylamine. This reaction has been used by Akiyama and Mine[3] for the determination of beryllium.

Procedure. Dilute approximately 20 ml. of molar beryllium nitrate solution to 30 ml. with water, and add 2 drops of bromothymol blue solution. Then add a solution of ethylamine or its carbonate until the indicator changes to blue. Shake and heat the solution on a steam-bath, maintaining the original volume by occasional additions of water. Discontinue heating when the odor of ethylamine is no longer observed. Filter off the precipitate, wash, dry and weigh as BeO.

Results obtained by this method are claimed to be very accurate.

Detection of hydrogen cyanide. Denigés[4] has proposed a method for detecting hydrogen cyanide which is based upon its catalytic effect in promoting the reaction between ammonia and alloxan to form characteristic crystals of oxaluramide. Kozlovskii and Penner[5] have shown that various amines, including ethyl amine, may be used in this test in place of ammonia.

1. A. W. Hofmann, *Ber.* 15, 767 (1882).
2. T. Kozu, *J. Chem. Soc. Japan.* 55, 437-46 (1934); *C.A.* 28, 4680 (1934).
3. T. Akiyama and Y. Mine, *J. Pharm. Soc. Japan.* 60, 309-11 (1940); *C.A.* 34, 7206 (1940).
4. G. Deniges, *Mikrochemie.* 4, 149-54 (1926); *C.A.* 21, 2628 (1927).
5. M. T. Kozlovskii and A. J. Penner, *Mikrochemie.* 21, 82-7 (1936); *C.A.* 31, 629 (1937).

ETHYLENEDIAMINE

Synonym: 1,2-Diaminoethane

$C_2H_8N_2$ Mol. Wt. 60.10 Beil. Ref. IV, 230.

$$H_2N—CH_2—CH_2—NH_2$$

Use: Detection of beryllium, cerium, lanthanum, magnesium, nickel, thorium, titanium and uranium.

Determination of antimony, bismuth, cadmium, cobalt, copper, mercury, nickel, silver and uranium.

Ethylenediamine is a colorless, clear, strongly alkaline liquid which has an ammoniacal odor. It has a sp. gr. of 0.898 and boils at 116-117° C. It is volatile in steam. The compound dissolves readily in water forming a hydrate and is also soluble in alcohol. It is only slightly soluble in ether and is insoluble in benzene. The monohydrate melts at 10° C. and boils at 118° C.

Preparation: Mix 42 g. of ethylene chloride with 510 ml. of aqueous 33 per cent ammonia, and heat for 5 hours in a closed tube at a temperature of 115-120° C. Remove the contents from the tube and evaporate until crystals begin to form, and then add 3 volumes of absolute alcohol. Wash the crystals with alcohol and decompose by distilling with the calculated quantity of powdered sodium hydroxide.[1-3]

Ethylenediamine may also be prepared by an application of Gabriel's synthesis, using phthalimide.[38]

Potassium phthalimide: Dissolve 200 g. of phthalimide in 4,000 ml. of alcohol, and add a solution of 76 g. of potassium hydroxide in 300 ml. of 75 per cent alcohol. Cool quickly, and filter off the crystals of potassium phthalimide. Heat the filtrate and add an additional 200 g. of phthalimide, and then 76 g. of potassium hydroxide in 300 ml. of 75 per cent alcohol. Again cool and filter. Stir the potassium phthalimide with sufficient acetone to form a thin paste and filter. Dry the product with gentle heating in air.[37]

Ethylenephthalimide: Heat 10 g. of potassium phthalimide with 12 g. of ethylene bromide for 2 hours at 200° C. Cool, and extract the residue by boiling with a dilute solution of sodium hydroxide. Filter off the oily residue, which solidifies on cooling, and dissolve it in 50 ml. of boiling alcohol. Cool and filter, and evaporate the filtrate to dryness. The residue is ethylenephthalimide.

Ethylenediamine: Mix 6.4 g. of ethylenephthalimide with a solution of 100-110 g. of potassium hydroxide in 300 ml. of water, and allow to stand two days with occasional shaking. Distill the resulting solution to dryness. Cool the residue and mix with 100 ml. of water, and again distill to dryness. Combine the distillates and neutralize with about 35 ml. of concentrated hydrochloric acid in 100 ml. of water. Evaporate to a volume of 100 ml. and filter. Again evaporate to a volume of 50 ml., and to the hot solution add 30 ml. of alcohol. Cool, filter, and again work up the mother liquor. The residue consists of ethylenediamine hydrochloride. Ethylenediamine hydrate, boiling at 118° C., is obtained by decomposing the hydrochloride with sodium hydroxide, distilling and drying with potassium hydroxide.[39]

In a later study, Putokhin [40] recommended grinding together 250 g. of potassium phthalimide with 130 g. of potassium carbonate, and heating this mixture with 190 g. of ethylene bromide to 185-195° C. Anhydrous ethylenediamine may be obtained by a method developed by Bailan.[41]

Determination of mercury. Mercury is completely precipitated as $[Cuen_2][HgI_4]$ by adding an excess of $[Cuen_2](NO_3)_2 \cdot 2H_2O$ to a neutral or slightly ammoniacal solution of a mercuric salt that has been treated with potassium iodide and heated to boiling. In the above formulas, and in similar formulas to follow, "en" represents ethylenediamine. Precipitation is complete in volumes ranging from 80-500 ml. of solution, even in the presence of considerable quantities of ammonium chloride or ammonium nitrate. It is essential to add sufficient potassium iodide to transform all mercury to the $[HgI_4]^=$ ion.[4-9] A large excess of potassium iodide is used.

Since precipitation of mercury by the above method is quantitative, this reaction may be used for the gravimetric determination of the metal:[4,5]

Reagent. The complex $[Cuen_2](NO_3)_2 \cdot 2H_2O$ is prepared by heating a mixture of 1 mole of cupric nitrate with 2 moles of ethylenediamine on a water-bath until a crust forms on the mixture.

A solution of the reagent can also be prepared by treating a solution of copper sulfate with ethylenediamine solution until the characteristic violet color of the complex is obtained. An excess of ethylenediamine does no harm.

Procedure. To 40-100 ml. of a neutral or slightly ammoniacal solution of a mercury salt, add an excess of potassium iodide and heat to boiling, and then precipitate with an excess of a boiling, concentrated solution of copper ethylenediamine nitrate. Stir well, allow to cool, and pour the mixture through a small filter crucible. Transfer the precipitate to the crucible with water containing 0.1 per cent of potassium iodide and 0.1 per cent of the precipitant. Wash the precipitate 3-4 times with this solution, then 3-4 times with 2-ml. portions of 96 per cent alcohol and finally 2-4 times with 2-ml. portions of ether. Dry the precipitate 15 minutes in a vacuum desiccator and allow to stand for 15 minutes in the balance case and weigh. The factor for mercury is 0.2249.

Straumanis and Cirulis[86] obtained favorable results using a somewhat similar procedure.

Mercury may also be determined titrimetrically by a procedure recommended by Spacu and Armeanu.[10] This method depends upon the precipitation of mercury as the violet colored $[Cuen_2][HgI_4]$ by means of the deep violet solution of copper ethylenediamine nitrate. The end-point is determined by the appearance of a violet color which is imparted to the solution from which precipitation occurs as soon as one drop of the reagent in excess has been added. Results have been obtained with an accuracy of about 0.3 per cent with this method. Mercury in any combined form may be determined by this method. Insoluble substances are dissolved in aqua regia, neutralized with ammonium hydroxide and then titrated with a solution of copper ethylenediamine nitrate that has been standardized against known quantities of mercury. Cyanides interfere with this method. Spacu and Murgulescu[11] have used a similar titration procedure except that the end-point is determined potentiometrically.

Determination of cadmium. Like mercury, cadmium is precipitated quantitatively in the presence of potassium iodide by adding a concentrated solution of copper ethylenediamine nitrate.[12,13]

Ammonium salts interfere in this procedure.

Reagent. For the method of preparing copper ethylenediamine nitrate, see determination of mercury.

Procedure. To 100-300 ml. of a neutral solution containing cadmium add an excess of potassium iodide and heat to boiling. Then add a hot concentrated solution of the reagent, stir well and cool completely. Filter and wash first with a solution containing 1 per cent potassium iodide and 0.3 per cent of copper ethylenediamine nitrate, and then wash 4-6 times with 2-ml. portions of alcohol and finally 3-4 times with 2-ml. portions of ether.

The factor for cadmium is 0.1396.

Determination of copper. When a neutral or a slightly acid solution of a copper salt is treated with ethylenediamine and potassium mercuric iodide, K_2HgI_4, in excess, a precipitate of $[Cuen_2][HgI_4]$ is formed. After washing and drying this precipitate may be weighed for the determination of copper.[14] A wash solution containing 1 per cent $K_2[HgI_4]$ is used; and finally the precipitate is freed from adhering wash liquid with alcohol and ether. The factor for copper is 0.07126.

Determination of bismuth. Bismuth is determined by treating a cold solution of the bismuth salt in dilute hydrochloric acid with an excess of potassium iodide and a concentrated solution of cobalt ethylenediamine chloride, $[Coen_3]Cl_3 \cdot 3H_2O$. A reddish-yellow precipitate of $[Coen_2]I \cdot [BiI_4]_2$ is formed which contains 23.24 per cent bismuth.[15,16]

Reagent. Mix a solution of 5 g. of purpureocobaltic chloride in 40 ml. of water with 5-8 g. of ethylenediamine and heat for a long time on a water-bath. The solution is gradually colored yellow to deep orange-yellow. When a test with alcohol yields a flesh colored precipitate and the supernatant liquid is only a weak rose color, discontinue the heating and allow the mixture to cool. Mix the solution with 250 ml. of absolute alcohol and filter the resulting precipitate with suction. Wash with 95 per cent alcohol and dry over sulfuric acid. The yield of the product may be increased by adding potassium iodide which precipitates cobalt ethylenediamine iodide, which may also be used as the reagent.[34]

Procedure. Treat the bismuth solution, which contains about 2 ml. of hydrochloric acid per 100 ml., with an excess of potassium iodide, and heat to boiling with a concentrated solution of cobalt ethylenediamine chloride. For each 0.1 g. of bismuth in 100 ml. of solution, use 0.3 g. of the reagent. Filter the reddish-yellow precipitate and transfer to the filter with a solution containing 0.1 g. of potassium iodide and 0.1 g. of cobalt ethylenediamine chloride in 100 ml. of water. Wash the precipitate with the same solution, and then wash 3 or 4 times with 2-ml. portions of 96 per cent alcohol. Finally wash with 1-2 ml. of ether. Dry in a vacuum and weigh. The factor for bismuth is 0.2324.

Spacu and Spacu[17,18] used a similar method for determining bismuth, but employed a concentrated solution of $[Coen_2(SCN)_2](SCN)$ as the precipitant. The precipitate consists of $[Coen_2(SCN)_2][BiI_4]$.

Reagent. The reagent is prepared from dichlorodiethylene cobalt chloride, which is prepared as follows: To a clear solution of 80 g. of crystallized cobalt chloride in 200 ml. of water, add a solution of 60 ml. of ethylenediamine hydrate dissolved in 40 ml. of water. Draw air through the brown-red liquid for 12 hours, and to the clear brown liquid add 400 ml. of concentrated hydrochloric acid. Heat the mixture for several hours to obtain a clear blue liquid. Allow to stand several days and separate the crystals of the hydrochloride by filtering on a funnel which is fitted with a fine platinum gauze. Use suction. Wash with concentrated hydrochloric acid, and then displace the acid by treating first with a mixture of equal volumes of absolute alcohol and ether and finally with absolute ether alone. The crystals are yellowish-green when pure. Dry over sulfuric acid for 24 hours.

Jorgensen[85] recommends mixing 48 ml. of ethylenediamine hydrate in 100 ml. of water to a filtered solution of 130 g. of cobalt chloride in 400 ml. of water to prepare the chloride. Air is drawn through this mixture for 12 hours, and the product is then treated as described above.

Cobalt diethylenediaminedithiocyanato thiocyanate is prepared as follows: Dissolve with gentle warming 40 g. of the above compound (which has been washed free of acid and dried at 100° C.) in 60 ml. of water and mix the warm solution with a similarly warmed solution of 40 g. of potassium thiocyanate in 30 ml. of water. A light green precipitate of the dichlorodiethylenediamine thiocyanate forms as a paste. Heat to boiling with stirring, whereupon the mixture becomes green-violet, and with further heating a dark violet and finally almost black compound is formed. On cooling the mass solidifies to a paste. With further boiling, the color changes to red, and the mixture solidifies to a mass of dull red-brown crystals. Dilute with 5-6 volumes of water, and dissolve most of the reaction product by gentle boiling. The insoluble residue consists of the dithiocyanatodiethylenediamine cobalt chloride. Purify by recrystallizing from water several times.

Mix an aqueous solution of this compound with potassium thiocyanate and heat a few minutes at a gentle boil. On cooling, a blood-red crystalline mass of the reagent separates. To recover more of the reagent, treat the mother liquor with more potassium thiocyanate and evaporate by boiling. Allow the solution to stand overnight and collect the crystals by filtration. Wash with water and purify by recrystallizing several times.[19]

Procedure. Heat 30 ml. of a solution containing 5-100 mg. of bismuth as the nitrate and as little nitric acid as possible, and add an excess of potassium iodide and a concentrated solution of the cobalt reagent. Allow the mixture to cool to room temperature and transfer the precipitate to a weighed Gooch crucible. Transfer the precipitate with a solution containing 0.3 g. of potassium iodide and 0.5 g. of $[\mathrm{Coen_2(SCN)_2}]\mathrm{SCN}$ in 100 ml. of water. Wash the precipitate with this same solution, being careful to use no more than a total of 10 ml. of this solution when the bismuth content is low. Next wash 3-4 times with a little 96 per cent alcohol and finally with 1-2 ml. of ethyl ether. Dry in a vacuum desiccator for 10 minutes and weigh. The factor for bismuth is 0.2065.

Determination of silver. Silver is determined by a reaction which is based upon the formation of the double salt, $[\mathrm{Ag(SCN)_2}][\mathrm{Coen_2(SCN)_2}]$. This is formed by adding potassium thiocyanate and $[Coen_2(SCN)_2](SCN)$ to a neutral or faintly acid solution of a silver salt.[20]

Reagent. The reagent is prepared as described under the determination of bismuth.

Procedure. To 70-100 ml. of a silver nitrate solution, which is neutral or faintly acid with nitric acid, add sufficient potassium thiocyanate to redissolve the silver thiocyanate which first forms. Heat to boiling and add a concentrated solution of the cobalt reagent and allow the mixture to cool. Filter off the reddish-orange precipitate and wash with a 1 per cent potassium thiocyanate solution containing 0.3-0.5 per cent of the cobalt reagent. Wash a few times with ethyl alcohol and finally with ether. Dry for 10 minutes in a vacuum desiccator and weigh. The factor for silver is 0.2078.

Results obtained by this method agree within 0.2 per cent of the theoretical value.

Determination of antimony. The compound $[Cren_3]SbS_4 \cdot 2H_2O$ is very stable and insoluble in water. It is formed by adding chromium ethylenediamine chloride, $[Cren_3]Cl_3 \cdot 3\frac{1}{2}H_2O$ to a solution of sodium thioantimonate, Na_3SbS_4. The compound precipitates in the form of lustrous yellow crystals, which may be washed with dilute ammonium hydroxide, then ethyl alcohol and ether and weighed. The precipitate is so voluminous that the determination is limited to approximately 0.05 g. of antimony. It is more rapid and convenient than the usual procedure of weighing as antimony sulfide: [21-23]

Reagent. Mix 8 g. of chrome alum, which has been dried at 100° C., with 6 g. of ethylenediamine in a flask fitted with an air condenser and heat the mixture on a water-bath. After a few hours a yellow to red mass is formed. Rub with a little water to form a paste. The yellow salt passes into solution and the red insoluble $[Cr_4(OH)_6en_6](SO_4)_3$ remains behind. Filter and mix the yellow solution with ammonium chloride to precipitate the reagent as a yellow solid. Purify by recrystallizing twice from warm water.[24]

Procedure. Mix the neutral or weakly acid, concentrated solution containing not more than 0.050 g. of antimony with dilute ammonium hydroxide until a faint ammoniacal odor persists. Heat almost to boiling, and add a few crystals of pure sodium sulfide in excess (0.5-1.0 g.). If the precipitate does not dissolve, add a few more crystals of sodium sulfide and heat to boiling. Add 5-6 drops of concentrated sodium polysulfide to clear the solution and heat for a short time. Dilute the solution (for 0.05 g. of antimony, dilute to 300 ml.), heat to 70-80° C. and add a three-fold excess of a cold reagent solution. Allow the mixture to cool and place the beaker in cold water. Cool for two hours and filter into a porcelain filtering crucible. Wash well with water, then 3-4 times with alcohol and finally 5-6 times with ether. Dry for 15 minutes in a desiccator over calcium chloride and weigh. The factor for antimony is 0.23494.

It is important in carrying out the precipitation that the temperature be kept below 70-80° C., since otherwise some chromic hydroxide is likely to precipitate.

Separation of nickel and cobalt. Weingarten [25] has used ethylenediamine for the separation of cobalt and nickel:

Procedure. To 50 ml. of a solution containing cobalt and nickel add ethylenediamine until the mixture is alkaline, and then add 5 ml. in excess. Add 10 ml. of hydrogen peroxide and after the reaction has subsided, add 3 g. of ammonium sulfate. Allow the mixture to stand for several minutes. If the mixture is red instead of pink after the hydrogen peroxide treatment repeat the treatment. The nickel complex separates as a violet precipitate while cobalt remains in solution. Filter and repeat the separation.

A fairly quantitative separation is obtained with a 0.01-0.1 N solution but not when the concentration is as great as 0.5 N.

Detection and determination of uranium. A bright yellow crystalline precipitate is obtained when a solution of ethylenediamine is added to a solution of a uranium salt. The precipitate is soluble in an excess of the reagent. Siemssen [26] reports that this reaction is as delicate as the ferrocyanide or hydrogen peroxide test for uranium.

The precipitate obtained when a 10 per cent solution of ethylenediamine is added to a solution of uranium salt settles rapidly and is easily filtered. When washed with cold water and ignited in a platinum crucible it may be weighed as U_3O_8. The solution from which precipitation takes place must be fairly concentrated, since otherwise the precipitate is gelatinous.[27]

Schwarz [28] has studied this method for determining uranium, but reports that it offers no advantage over a similar reaction employing ammonium hydroxide.

Detection of gold. Ethylene diamine reduces gold chloride to the metal to yield a yellow to dark brown color.[26,27] This reaction may be used for the detection of gold.

Detection of cerium, thorium, lanthanum and titanium. Solutions of cerium, thorium, lanthanum and trivalent titanium yield colored precipitates when treated with a little ammonium hydroxide and 10 ml. of a 1 per cent pyrogallol solution. Solutions of iron, chromium, aluminum, manganese, nickel, cobalt and uranium do not give color reactions when similarly treated. The reaction with cerium is a particularly delicate violet or dark blue precipitate. Shemyakin [29] has modified this reaction to use ethylenediamine instead of ammonium hydroxide.

Detection of magnesium. If the test for magnesium with naphthazarin or alkannin is carried out in a cold solution that has been made alkaline with sodium hydroxide, 0.5-1.0 mg. of magnesium gives a reaction. If ethylenediamine is substituted for sodium hydroxide, and the mixture is heated slightly, the test is 1000 times as sensitive.[30]

Detection of beryllium. Ethylenediamine is used as the alkaline reagent in the detection of beryllium with quinalizarin: [31]

Procedure. Mix 30 drops of a 0.05 per cent alcoholic quinalizarin solution with 5 drops of a 10 per cent ethylenediamine solution. In the presence of beryllium, the violet color turns blue. By the use of a blank as little as 0.14γ of beryllium can be detected.

Ethylenediamine is also used in a similar test with naphthazarin.

Detection and determination of thiosulfate. When a cold neutral or slightly alkaline solution of sodium thiosulfate is treated with an excess of a concentrated solution of nickel ethylenediamine nitrate, a violet crystalline precipitate of $[\mathrm{Nien_2}]\mathrm{S_2O_3}$ is formed. This compound is insoluble in cold water, difficultly soluble in hot water and almost insoluble in such organic liquids as ethyl alcohol, methyl alcohol, ether, chloroform and benzene. By means of this reaction as little as 0.04 mg. of thiosulfate can be detected.[32]

This reaction may be used in the presence of sulfide, sulfite, tetrathionate and thiocyanate. The reagent is prepared by adding ethylenediamine to a solution of nickel nitrate until a violet color is obtained. The reagent should contain 1 g. of the nickel ethylenediamine complex in 5 ml. of water.

Detection of nickel. The formation of the complex of $[\mathrm{Ni\ en_2}]\mathrm{S_2O_3}$ may also be used for the detection of nickel. This is accomplished by adding to the solution to be tested a few drops of ethylenediamine and a little sodium thiosulfate. This reaction is not nearly as sensitive as the dimethylglyoxime test, but it has the advantage that it can be used in concentrated solutions containing large quantities of iron, cobalt, copper, and chromium.[32]

Detection of acidity. Feigl and Barbosa[33] have used an ammoniacal or ethylenediamine solution of silver chromate as a sensitive reagent for acids. The reagent is prepared by digesting silver chromate with an insufficient quantity of ammonia or ethylenediamine for complete solution and then filtering the solution. The removal of any of the ammonia or ethylenediamine by reacting with hydrogen ions leads to the immediate precipitation of silver chromate. The use of an ammoniacal solution is not so satisfactory since ammonia escapes unless the vessel is tightly closed. A more stable solution is prepared by using ethylenediamine, which boils at 118° C. The vapor pressure in the silver chromate-ethylenediamine solution is so slight that the reagent can be kept for considerable periods without deterioration.

Reagent. Shake freshly precipitated, moist silver chromate continuously with an aqueous solution of ethylenediamine which is kept at a temperature of 60° C. From time to time add an additional portion of silver chromate until a considerable excess remains undissolved. Filter and allow the filtrate to stand for 12 hours. Filter, wash the crystals with ice-cold water and then dissolve in warm water. This solution is stable for weeks.

Procedure. Place 1 drop of the solution to be tested or a crystal of the solid material on a white spot plate and treat with 1-2 drops of the reagent. If an acid or a base-consuming compound is present, a brick red precipitate of silver chromate forms immediately.

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FUROACETYL-2,5-DIETHOXYANILINE

Use: Detection of uranium.

Detection of uranium. A solution of furoacetyl-2,5-diethoxyaniline in acetone yields a yellow color with as little as 0.03 mg. of uranium (as the uranyl ion) per ml. of solution. This reaction has been suggested by Clark and Stallings[1] for the detection of uranium.

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GUANIDINE CARBONATE

$C_3H_{12}O_3N_6$ Mol. Wt. 180.17 Beil. Ref. III, 86(39).

$$2HN{=}C(NH_2)_2\cdot H_2CO_3$$

Use: Detection of hypophosphates.

Determination of aluminum, beryllium, cadmium, cobalt, copper, magnesium, manganese, nickel, titanium and zinc.

Guanidine is a strong, mono-acid base whose aqueous solution is nearly as strong as that of sodium hydroxide.

Guanidine carbonate is a white crystalline solid. It melts at 197° C. Its sp. gr. is 1.25. It is freely soluble in water, but is insoluble in alcohol.

Preparation: Heat dry ammonium thiocyanate in a retort, fitted with a thermometer, for 20 hours at 180-190° C. Extract the mass with water, evaporate the aqueous solution somewhat, purify the crystalline salt (thiocyanate) with animal charcoal, and crystallize from water or alcohol. Dissolve 100 parts of the salt in the smallest possible quantity of hot water, and decompose with a concentrated solution of 58 parts of pure potassium carbonate. Concentrate the solution, first over a free flame, and then on a water bath, and finally heat the residue with 200 parts of alcohol. Filter hot the undissolved guanidine carbonate and crystallize from water.[1]

Precipitation of metals. Grossmann and Schuck[2] have used guanidine carbonate as a satisfactory precipitant for copper, nickel, cobalt, aluminum, cadmium, zinc, manganese, and magnesium. Copper, nickel, and cobalt are precipitated in the cold, but the precipitates are partially dissolved on warming. Aluminum salts give a white precipitate which dissolves in an excess of the reagent. Carbon dioxide is evolved and an aluminate is formed. Cadmium, zinc, manganese and magnesium are precipitated as carbonates with this reagent.

It is advantageous to use guanidine carbonate for precipitating the above metals, since the resulting precipitates are easily filtered. It is not so important to remove the last trace of the precipitant, since the reagent is easily volatilized.

Determination of beryllium and its separation from other metals. Jilek and Kota[3-6] have used guanidine carbonate for the gravimetric determination of beryllium in the presence of other metals. Interference by iron and aluminum is prevented by the formation of tartrate complexes; and if much ammonia is present, it is converted to hexamethylenetetramine by means of formaldehyde.

Reagents. *Ammonium tartrate solution:* Dissolve 42.5 g. of tartaric acid in water, add enough ammonium hydroxide to make the solution neutral to methyl red, and then dilute to 2 liters.

Guanidine carbonate solution: Dissolve 12 g. of guanidine carbonate in 300 ml. of water.

Procedure. To a solution containing not more than 0.1 g. of Al_2O_3 or 0.25 g. of BeO, add 50 ml. of ammonium tartrate solution. If the original solution contained much ammonium salts, add 5 ml. of 40 per cent formalin and sufficient 3 N sodium hydroxide to make the solution alkaline to phenolphthalein. Now make the solution faintly acid to methyl red and add 150 ml. of the guanidine carbonate solution. Stir well and dilute to 250 ml. Allow to stand 12-24 hours, filter, and wash the precipitate with a mixture of 50 ml. of the above tartrate solution, 150 ml. of the guanidine carbonate solution, and 2.5 ml. of 40 per cent formalin. Ignite, and weigh as BeO.

This method may be used for the separation of beryllium from cupric, ferric, uranyl, thoric, zirconic, thallous, tungstate, molybdate, chromate, arsenite, antimonite ions. The procedure is identical to that described above, except that after the addition of the ammonium tartrate, it is necessary when tungstates or vanadates are present to add dilute sodium hydroxide until the solution is alkaline to methyl red, and then to make the solution barely acid before adding the reagent.[3,4]

Determination of titanium and its separation from aluminum. Titanium is determined by the following procedure:[7]

Reagents. *Ammonium tartrate solution:* Dissolve 42.5 g. of tartaric acid in water, neutralize with ammonium hydroxide to methyl red, and then dilute with water to 2 liters.

Guanidine carbonate solution: Dissolve 8 g. of guanidine carbonate in 100 ml. of water and filter.

Procedure. To a solution containing not more than 0.6 g. of titanium chloride or sulfate in a porcelain dish, add 50 ml. of the ammonium tartrate solution. Neutralize with sodium hydroxide until the solution is barely acid to methyl red, and then add 75 ml. of the guanidine carbonate solution. Dilute the mixture to 400 ml., boil 5 minutes, and filter. Wash the precipitate with a hot, 1 per cent solution of ammonium acetate, dry, destroy the filter by heating with concentrated sulfuric and nitric acids, and ignite to constant weight. Weigh as TiO_2.

The method of Jilek and Kota [8] is satisfactory for precipitating titanium in the presence of aluminum. The method is also successful in the presence of chromate, tungstate, molybdate, and uranyl ions.

Separation of magnesium from alkalies. Hemming [9] has used guanidine for the precipitation of magnesium as magnesium hydroxide in the presence of the alkali metals.

Detection of hypophosphates. Solutions of soluble hypophosphates or hypophosphoric acid are precipitated with guanidine carbonate as the slightly soluble guanidine salt ($(CH_5N_3)_4 \cdot H_2PO_3 \cdot 5H_2O$). Only 1.038 g. of this salt dissolves in 100 ml. of solution. The formation of this precipitate serves to detect hypophosphoric acid in a mixture of the phosphorus acids.[10]

Reagent as an acidimetric standard. Dodd [11] recommends guanidine carbonate as a standard in acidimetry. It may be obtained in a pure state, it contains no water of hydration, and it is not hygroscopic. It reacts as a monoacid base when titrated with acids, using methyl orange, congo red, or alizarin red as indicator. Results obtained using this reagent are sufficiently accurate for routine work. Kling and Lassieur [12] report favorably on this reagent as a standard.

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TABLE 43.—REACTION OF GUANIDINE HYDROCHLORIDE WITH THE PLATINUM METALS

Test Material	Description
$RuCl_3$	Drop developed a green ring around the edge.
$RhCl_3$	No apparent reaction.
$PdCl_2$	No apparent reaction.
Na_3OsCl_6	After standing for some time, and as the drop evaporates many, deep-red, octahedra appear, first at the edge of the drop, then gradually throughout the entire drop. Many crystals formed in this test.
$IrCl_4$	Small very dark (purplish-red) octahedra form near the circumference of the drop.
H_2PtCl_6	Immediate formation of a great number of small yellow octahedra around test particle. These are smaller than when reagent is used as a solution although some larger crystals develop farther away from the test particle.
$AuCl_3$	Extremely long, slender needles form at the edge of the drop. These extend inward to and in some cases beyond the center of the drop.

GUANIDINE HYDROCHLORIDE

$CH_5N_3 \cdot HCl$ Mol. Wt. 95.54 Beil. Ref. III, 86.

$$NH{=}C(NH_2)_2 \cdot HCl$$

Use: Detection of gold, iridium, osmium, platinum and ruthenium.

Guanidine hydrochloride is a white crystalline powder. It dissolves readily in water and alcohol. The aqueous solution is neutral.

Preparation: Guanidine hydrochloride is prepared by neutralizing guanidine carbonate with hydrochloric acid.

Detection of the platinum metals. Whitmore and Schneider[1] have used guanidine hydrochloride as a microchemical reagent for the detection of the platinum metals. Results obtained by adding a solid fragment of the reagent to 2 per cent solutions of the platinum metal salts are given in Table 43, which is taken directly from the published work of these authors.

[1] W. F. Whitmore and H. Schneider, *Mikrochemie.* 17, 279-319 (1935).

p-HYDROXYPHENYLGLYCINE

Synonym: Photo-glycine

$C_8H_9O_3N$ Mol. Wt. 167.16 Beil. Ref. XIII, 488.

$$HOC_6H_4—NH—CH_2—COOH$$

Use: Detection of phosphorus and silicon.

Determination of iron, phosphorus and silicon.

p-Hydroxyphenylglycine is a solid compound. It darkens at 200° C., begins to melt at 220° C. and is molten at 247° C. with decomposition. It is slightly soluble in water and alcohol, but is insoluble in ether.

Preparation: Mix 188 g. of chloroacetic acid and 218 g. of *p*-aminophenol in an aqueous solution and allow to react at room temperature. Then add the resulting mixture slowly and in small portions to a second solution of 218 g. of *p*-aminophenol. Allow to stand for one-half hour and heat to boiling. The pure reagent separates from the solution.[1]

Detection and determination of silicon. *p*-Hydroxyphenylglycine may be used under suitable conditions of acidity and concentration as a reducing agent for the production of the blue color from the silicomolybdic acid complex. This reaction serves to detect 1 part of silicon in 100 million parts of water. DeEds and Eddy[2] have used this reaction for the colorimetric microdetermination of silicon.

Reagents. *p-Hydroxyphenylglycine reagent:* This is a 0.05 per cent solution of *p*-hydroxyphenylglycine in a 2.5 per cent solution of sodium sulfite. This reagent should be prepared daily.

Ammonium molybdate reagent: This reagent is a 2.5 per cent solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 0.1 N sulfuric acid. This solution should be prepared fresh daily.

Procedure. To 5 ml. of a solution containing 0.001-0.01 mg. of silicon, add 4 ml. of the molybdate reagent and mix well. Allow to stand for 10 minutes, add 30 ml. of water and again mix. Now add, with constant stirring, 2 ml. of *p*-hydroxyphenylglycine solution and allow the mixture to stand for 30 minutes for the development of the blue color. Transfer the solution to a 50-ml. Nessler tube, dilute to the mark, and measure the color in a photoelectric colorimeter. Compare with a calibration curve obtained with standard solutions of sodium silicate, silicon tetrachloride or sodium silicofluoride. Each ml. of the standard solution should contain 0.01 mg. of silicon.

Detection and determination of phosphate. Phosphorus may be detected and determined by the blue color which is obtained by treating a phosphomolybdate with *p*-hydroxyphenylglycine.[3]

Reagents. *Ammonium molybdate:* Dissolve 150 g. of ammonium molybdate in 1 liter of water with the aid of heat. Pour into a liter of nitric acid ($d = 1.20$) and allow to stand for several days in a moderately warm place. Decant the colorless liquid.

p-Hydroxyphenylglycine reagent: Mix 1 g. of *p*-hydroxyphenylglycine with 3-4 ml. of water and add just enough nitric acid ($d = 1.12$) to dissolve the solid. Dilute to 10 ml. with water.

Procedure. Mix 2 ml. of the ammonium molybdate reagent with 1 ml. of the *p*-hydroxyphenylglycine solution and carefully overlay with 0.1 ml. of a solution containing a phosphate. A green ring is formed which gradually changes to blue if the solution contains as little as 0.00005 mg. P_2O_5.

Hypophosphites and arsenic compounds do not give this reaction but ammonium salts and alkali hydroxides interfere. The blue color formed in this reaction may be used for the colorimetric determination of phosphates in fertilizers. Comparison is made with standards prepared from monopotassium phosphate and of approximately the same phosphate concentration as the solution to be analyzed. About 15 minutes are required for the development of the maximum color intensity. Iron causes no appreciable error if the ratio of P_2O_5 to Fe_2O_3 is not less than 0.2.

This reaction has also been used for the determination of phosphates in blood.[4]

Determination of iron. *p*-Hydroxyphenylglycine has been recommended as one for the better reducing agents for converting ferric iron to ferrous iron as a preliminary to the colorimetric determination of iron with 2,2′-dipyridyl.[5,6]

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HEXAMETHYLDIAMINOISOPROPANOLDIIODIDE

Synonym: Iodisane

$C_9H_{24}ON_2I_2$ Mol. Wt. 418.11

$HO—CH(CH_2—N(CH_3)_3I)_2$

Use: Detection of cadmium.

Iodisane is a white crystalline powder which melts at about 275° C. with decomposition. It dissolves readily in water, but is only slightly soluble in alcohol. It is insoluble in ether and acetone. It is generally supplied in the form of a 20 per cent solution in ampules.

Detection of cadmium. A drop of a cadmium solution reacts with iodisane to give a characteristic precipitate which may be used to detect as little as 1γ of cadmium at a dilution of 1:50,000. Zinc salts in concentrations as high as 10 per cent give no precipitate. On evaporation, however, crystals similar to those obtained with cadmium are obtained. Ferric iron interferes with this test.[1,2]

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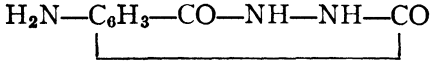
LUMINOL

Synonym: *o*-Aminophthalhydrazide

$C_8H_7O_2N_3$ Mol. Wt. 177.14



$H_2N—C_6H_3—CO—NH—NH—CO$

Use: Detection of copper, cyanide, iron and peroxide.

Luminol is a white to yellow solid melting at 319-320° C.

Preparation: *3-Nitrophthalhydrazide:* Dissolve 130 g. of hydrazine sulfate and 272 g. of crystallized sodium acetate in 400 ml. of hot water, and add the clear solution to 211 g. of solid 3-nitrophthalic acid contained in a 20-cm. porcelain evaporating dish. Evaporate over a free flame as rapidly as possible with constant stirring. Grind the residual solid to a fine powder, place in a beaker and heat for 3 hours at 150-170° C. in a suitable oil bath. Stir frequently, and if the material cakes, remove and powder. Measure the temperature of the heated powder and not externally. At the end of the heating period, powder the solid, and extract twice with 350 ml. of hot water to remove sodium sulfate. Dry the residual solid at 105° C. to constant weight.

3-Aminophthalhydrazide: Add gradually and in small portions 192.5 g. of the crude product obtained above to 1 liter of 6 N ammonium sulfide solution. This is prepared by saturating 200 ml. of concentrated ammonium hydroxide with hydrogen sulfide in the cold, then adding an additional 200 ml. of ammonium hydroxide, and finally diluting to 1 liter. Reduction is vigorous, and the flask may require external cooling. After all the solid 3-nitrophthalhydrazide has been added, keep the resulting mixture at the boiling point for 1 hour while passing in hydrogen sulfide gas. After adding the hydrogen sulfide, boil for an hour or more, and allow to stand until cold. Filter with suction, wash thoroughly with water and dry. Acidify the filtrate with a slight excess of glacial acetic acid and filter. Wash the precipitate with water and dry.

The precipitate consists of free sulfur and 3-aminophthalhydrazide. To free the reagent from sulfur, stir the crude mixture with a quantity of 5 per cent sodium hydroxide which is just sufficient to form the sodium salt ($C_8H_6N_3O_2Na$), assuming no sulfur is present. Stir and warm slightly, and then filter. Cool to 0° C., and stir and scratch the walls of the container. When precipitation is complete, filter with suction, and press as dry as possible on filter paper. Dissolve the solid in water, and precipitate by adding a slight excess of glacial acetic acid. Filter with suction, wash free of sodium acetate with water, and dry.[1]

Detection of hydrogen peroxide. Luminol, described by Albrecht,[2] was first used by Harvey[3] for the detection of peroxides. More recently Druckery and Richter[4,5] and Steigmann[6] have studied this reaction. The test is indicated by the appearance of a blue-violet luminescencc produced by hydrogen peroxide in alkaline solutions of luminol. This same luminescence is observed during hydrolysis of esters; the reaction between acids and bases; the addition of concentrated alkali solutions; heating; during the solution of substances; and in the dilution of concentrated salt solutions. In each of the above cases oxygen is essential.

Reagents. *Luminol solution:* Dissolve 0.1 g. of luminol in 10 ml. of concentrated ammonium hydroxide and dilute with water to 100 ml.

Copper sulfate solution: Dissolve 0.1 g. of copper sulfate in 20 ml. of water and 5 ml. of concentrated ammonium hydroxide and dilute with water to 200 ml.

Sodium persulfate solution: A freshly prepared 10 per cent solution of sodium persulfate in water.

Procedure. Just before making the test for hydrogen peroxide, mix 1 ml. of the luminol solution with 5 ml. of water, add 0.25 ml. of the copper sulfate solution, and then add 2 ml. of the sodium persulfate solution. This mixture glows with a bluish-violet luminescence in the presence of as little as 0.2 g. of hydrogen peroxide in 8.75 ml. of solution. The mixture also glows very slightly due to the persulfate.

This reaction may also be carried out as a spot test.

Procedure. Dilute 1 drop of luminol solution (above) with 1 drop of water and place the mixture on a sheet of copper which has been cleaned with soap, rinsed with water and dried. Then in a dark room add 1 drop of the solution to be tested. The luminescence is observed at a dilution limit of 1:1,000,000.

Ascorbic acid, cystine, and hydroquinone interfere with the hydrogen peroxide reaction. Glucose and fructose in strongly alkaline solutions produce luminescence by the auto-oxidation of luminol. Solutions of succinates also have this effect after long standing, but freshly prepared solutions of succinate are inactive. Acetic acid behaves similarly and ethyl alcohol also produces luminescence.

Detection of iron and copper. By suitable modifications of the above procedure, ferric ion, copper and cyanide may be detected.[6]

Procedure. To 0.5 ml. of a reagent prepared by mixing 1 ml. of the luminol solution (above), 4 ml. of water, and 0.5 ml. of 3 per cent hydrogen peroxide contained in a small test tube, add the copper or ferric salt solution to be tested. With copper the familiar bluish-violet luminescence appears, and with iron short flashes are observed. As little as 0.13γ of copper (dilution limit 1:2,500,000) and 0.25γ of iron (dilution limit 1:2,500,000) can be detected.

Detection of cyanide. A modification of the luminol test serves to detect small quantities of cyanides.

Procedure. To each of two small test tubes, add 0.1 ml. of 1:100,000 solution of crystalline copper sulfate for determining cyanides near the dilution limit (dilution limit 1:250,000), and a more concentrated copper sulfate solution if the cyanide is less dilute. The sensitivity of this reaction is 0.8γ of cyanide ion.

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METHYLAMINE

CH_5N Mol. Wt. 31.06 Beil. Ref. IV, 32.

$$CH_3—NH_2$$

Use: Detection of iridium, nickel, platinum, ruthenium and silver.

Determination of aluminum.

Methylamine is a colorless inflammable gas at ordinary temperature and pressure, and has a strong ammoniacal odor. It is a stronger base than ammonia. One volume of water at 25° C. dissolves 959 volumes of the gas. The compound is usually marketed in a liquefied form, or as a 33 per cent aqueous solution.

Preparation: Mix 30 g. of acetamide and 26 ml. of bromine in a 500-ml. flask, and while cooling the mixture with water, add a sufficient quantity of a solution of 50 g. of potassium hydroxide and 350 ml. of water until the color of the solution is pale yellow. Transfer this solution to a dropping funnel, and allow to flow in an unbroken stream into a solution of 80 g. of potassium hydroxide dissolved in 150 ml. of water which is maintained at 70-75° C. in a 1-liter flask. Keep the temperature at 70-75° C. for about 15 minutes, or until the reaction mixture is colorless, and then distill the methylamine with steam. Fix an adapter to the lower end of the condenser and allow this to extend about 1 cm. below the surface of 100 ml. of approximately 5 N hydrochloric acid. Continue the distillation until the distillate is no longer alkaline, and then evaporate the solution in the receiver to dryness in a porcelain dish on a water bath. Allow the dish to stand overnight in a vacuum desiccator to remove the last traces of moisture. Dissolve the methylamine hydrochloride by boiling the dried material with absolute alcohol. Filter and concentrate the filtrate to a small volume to obtain crystals of the methylamine hydrochloride. Filter with suction, wash with a little alcohol, and dry in a desiccator. The free amine is obtained by treating the hydrochloride with a base.[1]

Detection of nickel. Nickel may be detected by means of the blue color which is obtained when the anhydrous sulfate, nitrate, or chloride is heated with methylamine hydrochloride.[2-4] The following procedure is used.

Procedure. Heat a little powdered anhydrous nickel sulfate, nitrate, or chloride in a porcelain dish with about the same quantity of completely dry methylamine hydrochloride. A blue color results, and this disappears when the mixture is allowed to cool, leaving a dirty grayish-yellow mass. This soon takes up atmospheric moisture and deliquesces. The above reaction is sensitive to about 0.1 mg. of nickel.

Anhydrous cobalt salts give an intense blue, oily drop, but this may be differentiated from the color due to nickel, since the former does not lose its color on cooling.

Silvestri and Cappelli [3] have used this reaction for the detection of nickel on nickel plated objects. The plated surface is treated with a few drops of concentrated hydrochloric acid, and a small crystal of methylamine hydrochloride is added to the resulting solution. Upon heating, a blue color appears as described above. This disappears on cooling. No other common metal behaves in a similar manner.

Detection of silver. Martini [5] has used methylamine as a sensitive microchemical reagent for the detection of silver.

Procedure. Place 1 drop of a 1 per cent solution of silver nitrate, or of the solution to be tested, on an object glass and mix with a drop of acetic acid. Then add a drop of methylamine solution. The latter drop is placed with the aid of a glass rod very close to the edge of the mixture of silver nitrate and acetic acid. A white crystalline precipitate of silver and methylamine acetate appears at the point where the two drops are in contact.

The sensitiveness of this reaction is 0.01γ of silver. Lead and mercuric ions also give precipitates under conditions of the test, but these need not be confused with the silver test. Silver may be determined in the presence of

100 times as much mercury and 1000 times as much lead, and in the presence of both lead and mercury when the ratio of silver:lead:mercury = 1:100:100.

Detection of ruthenium and iridium. Whitmore and Schneider[6] have used methylamine hydrochloride as a sensitive microchemical reagent for ruthenium and iridium. This reagent may be added to the test drop in the form of a 10 per cent solution, or preferably as a solid fragment. On standing for a short time, a deep green ring forms around the circumference of a drop containing ruthenium. After the drop evaporates the reagent forms about the edge as large cubes, which acquire a very bright green color. This test may be used in the presence of all other elements of the platinum group, and appears to be very satisfactory even in mixtures consisting of all of the ions of this group.

Iridium may also be determined by means of methylamine hydrochloride. When a solid fragment of the reagent is added to a drop of the test solution and the drop allowed to evaporate, deep red octahedra or lighter red plates are formed around the crystals of the reagent if iridium chloride is present. This test may be observed while carrying out the procedure for ruthenium. This reaction may also be used for platinum if iridium is absent. In this case small, bright yellow, well-formed octahedra indicate the presence of platinum.

These tests are summarized in Table 44, which is taken from the work of Whitmore and Schneider.[6]

TABLE 44.—REACTIONS OF IRIDIUM AND PLATINUM WITH METHYLAMINE HYDROCHLORIDE
Test Material 1% Solution
Reagent Methylamine Hydrochloride—Solid Fragment

Test Material	Description
$IrCl_4$	A number of deep red hexagonal plates are formed throughout the drop. Also a great number of very small dark, almost black, octahedra.
H_2PtCl_6	A precipitate is formed immediately which consists of small bright yellow octahedra. These are particularly well developed and grow to a large size near the circumference.
	A few yellow hexagonal plates are also formed.
	Other metals give no test.

Determination of aluminum. Kozu[7] has used a solution of methylamine or a methylamine solution saturated with carbon dioxide for the precipitation of aluminum.

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5. A. Martini, *Mikrochemie.* 7, 231 (1929).
6. W. F. Whitmore and H. Schneider, *Mikrochemie.* 17, 279-319 (1935).
7. T. Kozu, *J. Chem. Soc. Japan.* **55**, 447-57 (1934) ; *C.A.* **28**, 4680 (1934).

METHYLANILINE

Synonym: Monomethylaniline

C_7H_9N Mol. Wt. 107.15 Beil. Ref. XII, 135.

$C_6H_5NH(CH_3)$

Use: Detection of gold, iridium, osmium, palladium, platinum, rhodium and ruthenium.

Methylaniline is a colorless or slightly yellow liquid, which becomes brown on exposure to air. It has a sp. gr. of 0.989 and boils at 192° C. It is only slightly soluble in water, but dissolves in alcohol and ether.

Preparation: Mix 25 ml. of water and 10 g. of aniline, and add alternately with shaking and in small portions 20.5 g. of *p*-toluenesulfonchloride and 82 ml. of 10 per cent aqueous sodium hydroxide. To the resulting clear solution add 10 ml. of dimethyl sulfate and shake. Crystals of *p*-toluenesulfonic acid methylanilide separate. An additional quantity of the anilide may be recovered by adding sodium hydroxide to the mother liquor. Saponify 27 g. of the anilide by heating for 3 hours on a water bath with 34 ml. of concentrated sulfuric acid and 13.5 ml. of glacial acetic acid. Finally heat for a short time at 120° C. Dilute the mixture with water, make alkaline and extract the reagent with ether.[1]

Detection of platinum metals. Whitmore and Schneider[2] have studied the use of methylaniline as a microchemical reagent for the platinum metals. Their results, which are obtained by adding the reagent to 2 per cent solutions of the platinum metal salts, are given in Table 45.

TABLE 45.—REACTIONS OF THE PLATINUM METALS WITH METHYLANILINE

Test Material	Description
$RuCl_3$	A green, flocculent precipitate surrounds the reagent particle immediately.
$RhCl_3$	A scant, green flocculent precipitate forms around the reagent particle.
$PdCl_2$	An exceedingly dense mass of irregular crystalline structures surrounds the reagent particle immediately. At the edge of this precipitate many small, bright-yellow rectangular prisms, some with pointed ends, appear.
Na_2OsCl_6	A green, flocculent precipitate forms immediately. On standing some bright yellow irregular crystalline structures develop throughout this precipitate.
$IrCl_4$	A green, flocculent precipitate forms immediately.
H_2PtCl_6	Irregular greenish-yellow, branching, crystalline structures develop immediately. A few hexagonal plates, greenish-yellow in color also appear.
$AuCl_3$	A bright-green, flocculent precipitate forms immediately. A great many small black granules also appear which seem to be metallic particles.

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1. F. Ullmann, *Ann.* 327, 110 (1903).
2. W. F. Whitmore and H. Schneider, *Mikrochemie.* 17, 279-319 (1935).

MORPHOLINE

Synonym: Diethyleneimide oxide

C_4H_9ON Mol. Wt. 87.12 Beil. Ref. XXVII, 5.

$$O{=}(CH_2{-}CH_2)_2{=}NH$$

Use: Detection of gold.

Determination of copper and zinc.

Morpholine is a colorless hydroscopic oil. It has an odor similar to that of ammonia and exhibits alkaline properties. It boils at 128-129° C. and has a sp. gr. of 0.999. It is miscible with the common solvents.

Preparation: Dissolve diethanolamine in 5-10 times as much 70 per cent sulfuric acid and heat for 8 hours at 160-170° C. Cool, and carefully neutralize the contents of the tube with concentrated sodium hydroxide. Then make strongly alkaline by the addition of solid sodium hydroxide and distill with steam. Volatile morpholine is in the first part of the distillate. Evaporate the distillate with hydrochloric acid on a water-bath and decompose the hydrochloride with sodium hydroxide. Morpholine separates as an oily liquid. Take up with ether and dry with solid potassium hydroxide. Remove the ether by distillation.[1,2]

Determination of zinc and copper. Morpholine precipitates as the hydroxides the same metals as ammonium hydroxide, but unlike the latter it does not form soluble complexes. Precipitates of copper and zinc are therefore insoluble in an excess of the reagent. Soluble compounds are formed only with amphoteric hydroxides. Precipitates at normal temperatures are crystalline, easily filterable and readily washed free of impurities. Morpholine is used advantageously for precipitating metals, since, like ammonia, it is completely volatile at higher temperatures and does not cause contamination of the precipitate.

When an aqueous solution of morpholine is added to solutions of zinc and copper salts, precipitates are formed which when washed with hot water containing a little morpholine, yield pure zinc oxide and copper oxide upon ignition.[3]

Procedure. To 50 ml. of a solution containing about 0.5 g. of zinc as zinc chloride, add a 25 per cent aqueous solution of morpholine until the reaction mixture is distinctly alkaline. Allow to stand for one-half hour and filter. Wash with hot water containing a little morpholine. Dry, ignite and weigh as zinc oxide.[3]

Copper is determined in a similar manner.

Detection of gold. Malowan[4] has used the reducing properties of morpholine for the detection of gold.

Procedure. To 2-3 ml. of the solution to be tested, add 0.3 ml. of pure morpholine, or a sufficient quantity to make the mixture distinctly basic. Filter to remove any precipitate of copper, iron or zinc. Heat the filtrate to boiling. If gold is present, the solution is yellow in color and gradually assumes a bluish-violet tint. A bluish-violet precipitate may separate if the quantity of gold is great enough. An approximate determination is made by comparing the appearance of the test solution with that of solutions containing known quantities of gold.

1. L. Knorr, *Ber.* **22**, 2084 (1889).
2. L. Knorr, *Ann.* **301**, 1, 2 (1898).
3. L. S. Malowan, *Mikrochemie.* **26**, 319-21 (1939); *C.A.* **33**. 4901 (1939).
4. L. S. Malowan, *Z. anal. Chem.* **118**, 100-2 (1939); *C.A.* **34**, 2277 (1940).

1,8-NAPHTHALENEDIAMINE

$C_{10}H_{10}N_2$ Mol. Wt. 158.18 Beil. Ref. XIII, 205.

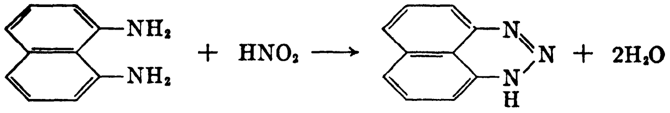
$C_{10}H_6(NH_2)_2$

Use: Detection of nitrite and selenium.

1,8-Naphthalenediamine is obtained as a crystalline solid from water and alcohol. It melts at 66.5° C. and boils at 205° C. It gradually turns brown on standing. The compound is soluble in both alcohol and ether.

Preparation: Grind 2 g. of 1,8-dinitronaphthalene with 20 g. of phosphorus triiodide, mix with 16 ml. of water and quickly transfer to a 300-400 ml. beaker. On standing for 1 or 2 minutes, or on warming on a water-bath, a reaction takes place almost instantaneously and with some violence. When the reaction is ended add 24 ml. of water and boil. All the solid dissolves except a small residue. Filter hot and allow to cool to obtain crystals of 1,8-naphthalenediamine hydroiodide. Convert the hydroiodide to the free base by adding a concentrated solution of sodium hydroxide until the mixture is weakly alkaline. Filter, wash with cold water, and dissolve in alcohol. Precipitate the reagent by adding a double quantity of water.[1]

Detection of nitrite. 1,8-Naphthalenediamine reacts with nitrites in acid or neutral solutions to form an orange-red precipitate of 1,8-aziminonaphthalene. This reaction takes place according to the following equation:[2]

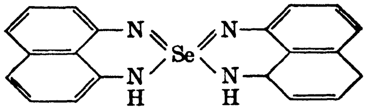


This reaction may be used for the detection of small quantities of nitrous acid.[3]

Procedure. Mix a drop of the solution to be tested with 1 drop of a 0.1 per cent solution of 1,8-naphthalenediamine in 10 per cent acetic acid. An orange-red precipitate or coloration, depending upon the nitrite content, appears immediately or after warming. By means of this reaction 0.1γ of nitrous acid can be detected at a concentration of 1:500,000.

Selenious acid reacts with 1,8-naphthalenediamine to form a brown precipitate, but other acids such as sulfuric acid yield colorless insoluble salts.

Detection of selenious acid. When a solution of selenious acid or an alkali selenite is heated with 1,8-naphthalenediamine in an acetic acid solution, a brown insoluble precipitate is formed.[4] When an excess of the reagent is used, this compound consists essentially of di-peri-naphthoseleniumdiazole:[5]



This reaction is specific for selenites in the absence of nitrites, and can be carried out as a spot test. In this way 1γ of SeO_2 is detected.

1. R. Meyer and W. Muller, *Ber.* 30, 775 (1897).
2. A. de Aguiar, *Ber.* 7, 315 (1874).
3. F. Feigl, *Qualitative Analysis by Spot Tests*, 2nd English Edition, p. 216, Nordemann, New York (1939).
4. F. Sachs, *Ann.* 365, 150 (1909).
5. O. Hinsberg, *Ber.* 52, 21 (1919).

NAPHTHIONIC ACID

Synonym: Piria acid, α-naphthylamine-*p*-sulfonic acid, 4-aminonaphthalene-1-sulfonic acid

$C_{10}H_9O_3NS$ Mol. Wt. 223.23 Beil. Ref. XIV, 739.

$$H_2N—C_{10}H_6—SO_3H$$

Use: Detection of nitrite.

Determination of aluminum, nitrite and potassium.

Naphthionic acid is a white to slightly reddish-yellow crystalline solid. It is only very slightly soluble in water, alcohol and ether, but dissolves in solutions of the alkali hydroxides or carbonates with strong blue fluorescence.

Preparation: Add finely ground and well-dried α-naphthylamine hydrochloride in small portions to fuming sulfuric acid (20-25 per cent SO_3) which is well-cooled by immersing in an ice-bath. The salt dissolves with the evolution of hydrogen chloride. Interrupt the reaction when sufficient α-naphthylamine hydrochloride has been added to react with the sulfur trioxide, and then pour the reaction mixture onto crushed ice. The free acid separates as a curdy precipitate. Filter, wash with water, convert to the calcium salt, and then convert this to the sodium salt with sodium carbonate. Filter and evaporate the solution of the sodium salt to a syrupy consistency and cool. Press out the separated salt, dissolve in alcohol, filter, and distill off the alcohol. Recrystallize the product several times from water. Remove the supernatant liquid quickly and dry in a vacuum at ordinary temperature. The free acid is precipitated by treatment with mineral acids.[1]

Detection and determination of nitrites. Riegler [2-5] and Vaubel [6] have used naphthionic acid as a sensitive reagent for the detection and determination of nitrites.

Procedure. Mix 20-30 mg. of naphthionic acid with about 5 ml. of the solution to be tested and add 3 drops of concentrated hydrochloric acid. Shake vigorously for about 1 minute and carefully overlay with 20 or 30 drops of ammonium hydroxide. If nitrites are present a rose-red ring forms at the junction of the two liquids. Upon mixing thoroughly the liquid is colored rose to dark red.

Riegler [8] has used this reaction for the colorimetric determination of small quantities of nitrites in water.

Procedure. To 100 ml. of the water to be analyzed, containing about 0.001 g. of N_2O_3, add about 0.05 g. of naphthionic acid and 5-6 drops of concentrated hydrochloric acid. Shake well and add 30 drops of concentrated ammonium hydroxide solution. Mix well and compare the resulting rose color with that of standard solutions containing known quantities of nitrite.

Approximately 0.01 mg. of N_2O_3 in 100 ml. of solution may be determined by the above procedure.

According to Riegler [4,9] commercial samples of naphthionic acid vary somewhat in their properties, and consequently the reagent is not wholly satisfactory for the detection and determination of nitrites. Accordingly a new reagent, which is claimed to be twenty times as sensitive, has been prepared.

Reagent. Add 2 g. of pure sodium naphthionate and 1 g. of β-naphthol to 200 ml. of water and shake vigorously. Filter and use the clear filtrate as the reagent.

Procedure. To 10 ml. of the solution to be tested, add 10 drops of the reagent and 2 drops of concentrated hydrochloric acid. Shake vigorously and overlay with 20 drops of ammonium hydroxide. At the zone of contact of the two liquids a red colored ring appears. On shaking, or simply on standing, the entire liquid becomes rose to red in color. By this reaction 1 part of nitrite in 10,000,000 parts of solution can be detected.

To determine nitrites with the above reagent proceed as follows:

Procedure. To 100 ml. of solution containing about 0.1 mg. of N_2O_3, add 20-30 drops of the sodium naphthionate-β-naphthol reagent and 4 drops of concentrated hydrochloric acid. Shake well and add 20 drops of concentrated ammonium hydroxide. Compare the resulting rose-red color with that of standard solutions containing known quantities of nitrite.

By the above procedure 0.05 mg. of N_2O_3 per liter can be determined.

A solid reagent prepared by mixing equal parts of naphthionic acid and β-naphthol may be used.

Determination of aluminum. Schams [7] has used naphthionic acid as an auxiliary reagent for the colorimetric determination of aluminum after precipitating with 8-hydroxyquinoline. The aluminum is first precipitated with 8-hydroxyquinoline, and the precipitate is then coupled with diazotized naphthionic acid to form a dyestuff having a color similar to that of the permanganate ion. This reaction has been used for the microcolorimetric determination of aluminum in plant ash. If more than 0.02 mg. of aluminum is present results are obtained which are accurate to within 2 per cent of the quantity present. The method may be used to determine as little as 10γ of aluminum in 200 ml. of solution. For details of the procedure see section on 8-hydroxyquinoline.

Determination of potassium. Tischer[8,10,11] has used sodium naphthionate for determining 0.001-1.0 mg. of potassium. The potassium is first precipitated as $K_2NaCo(NO_2)_6$, which after washing is dissolved in hot water, and the nitrite determined as described above. As a reagent Tischer recommends a solution of 5 g. of sodium naphthionate and 2.5 g. of β-naphthol in 500 ml. of water.

1. O. N. Witt, *Ber.* **19**, 578 (1886).
2. E. Riegler, *Z. anal. Chem.* **35**, 677 (1896).
3. E. Riegler, *Z. anal. Chem.* **36**, 306 (1897).
4. E. Riegler, *Z. anal. Chem.* **36**, 377 (1897).
5. D. De Paepe, *Bull. assn. Belge des chimistes.* [3] **12**, 98 (1898).
6. W. Vaubel, *Chem.-Ztg.* **52**, 842 (1928); *C.A.* **23**, 792 (1929).
7. O. Schams, *Mikrochemie.* **25**, 16-46 (1938); *C.A.* **33**, 1628 (1939).
8. J. Tischer, *Biochem. Z.* **238**, 148-61 (1931); *C.A.* **25**, 5641 (1931).
9. W. Autenrieth and A. Funk, *Z. anal. Chem.* **52**, 137-67 (1917); *C.A.* **7**, 3627 (1913).
10. F. Alten and H. Weiland, *Z. Pflanzenernahr., Dungung Bodenk.* **34A**, 108-10 (1934).
11. F. Alten, H. Weiland and B. Kurmies, *Z. Pflanzenehnahr., Dungung Bodenk.* **32A**, 171-82 (1933).

α-NAPHTHYLAMINE

Synonym: 1-Aminonaphthalene

$C_{10}H_9N$ Mol. Wt. 143.18 Beil. Ref. XII, 1212.

$$C_{10}H_7—NH_2$$

Use: Detection of ammonia, chromium, copper, gold, mercury, nitrate, nitrite, oxygen, ozone and thallium.

Determination of chromium, copper, gold, iodine, mercury, nitrate, nitrite, potassium, sodium, and tungsten.

α-Naphthylamine is a white crystalline solid which turns red on exposure to air. It possesses an unpleasant odor, is volatile with steam and may be sublimed. It melts at 50° C. and boils at 301° C. It is only slightly soluble in water, but dissolves readily in alcohol and ether.

Preparation: Place 120 g. of powdered iron and 60 ml. of water in a vessel equipped with a stirrer and heat to 95° C. Add 10 ml. of concentrated hydrochloric acid, and pour in gradually 100 g. of α-nitronaphthalene. Continue the reduction until the sample is completely soluble in hydrochloric acid. Steam distill with superheated steam. Filter off the product and crystallize from benzene or toluene.[87]

Detection of nitrite. The red azo derivative of sulfanilic acid was first prepared by Roussin[1] in 1878, and soon afterward the formation of the compound was recommended by Griess[2] as a sensitive test for nitrous acid. According to Griess, the solution containing the nitrite is acidified with sulfuric acid and then treated with a solution of sulfanilic acid. After a few moments a solution of α-naphthylamine sulfate is added. A red color is formed in the presence of a trace of nitrite. In the presence of nitrite, sulfanilic acid is converted by the nitrous acid into the corresponding diazo compound, and the latter then couples with α-naphthylamine to form α-naphthylamine-*p*-azobenzene-*p*-sulfonic acid, a red azo dye.

The Ilosvay modification of the nitrite test requires two solutions, prepared as follows:

Reagent A: Dissolve 0.5 g. of sulfanilic acid in 150 ml. of dilute acetic acid.

Reagent B: Boil 0.1 g. of α-naphthylamine with 20 ml. of water and decant the colorless solution from the residue, and add to the solution 150 ml. of dilute acetic acid.

Procedure. Add a few ml. of reagent A to 20 ml. of the solution to be tested and warm to about 75° C. Then add a few ml. of reagent *B*. A red color is obtained if nitrite is present. This reaction is sensitive to 1 part in 1 billion.

Lunge and Lwoff[11-18] prepared the nitrite reagent as follows:

Reagent. Dissolve 0.1 g. of α-naphthylamine in 100 ml. of boiling water and add 5 ml. of glacial acetic acid. Then add a solution of 1 g. of sulfanilic acid in 100 ml. of water.

Tschirikow[19] recommends the following procedure for the test:

Procedure. Add 5 drops of hydrochloric acid and 5 drops of saturated sulfanilic acid solution to 100 ml. of the solution to be tested. Allow to stand 5 minutes and add 5 drops of a saturated α-naphthylamine solution.

Hahn[25] has prepared a test paper for nitrites by using α-naphthylamine oxalate.

Reagent. Dissolve 1 part oxalic acid in alcohol by warming on a waterbath, and add 1 part of α-naphthylamine, also dissolved in a little alcohol. Filter the crystals of α-naphthylamine oxalate which separate. Wash with a little alcohol and ether, and dry in a vacuum over sodium hydroxide.

Soak filter paper in a solution of 100 ml. of hot distilled water containing about 1 g. of α-naphthylamine oxalate and pure sulfanilic acid and 0.2 g. of potassium oxalate. A solution containing as little as 0.05γ of nitrite per ml. is detected by the red color which forms when applied to the test paper.

Salei[26] has used for the determination of nitrite a dry reagent consisting of α-naphthylamine, sulfanilic acid and succinic acid.

α-Naphthylamine reacts alone with nitrous acid to form a diazo compound which may be coupled with many phenols and amines to give sensitive color reactions. A number of these have been studied and reported by Dubsky and Okac.[27] These results are shown in the section on dyes.

The Griess reaction, or some modification of it, is extensively used in qualitative procedures for the detection of the nitrite ion.[30-35] One of the most satisfactory of the various modifications of the Griess reaction is that obtained by coupling diazotized α-naphthylamine and β-naphthylamine-6,8-disulfonic acid (Amino-*G*-acid) to give a violet-blue dye in an acid solution.[28] This reaction is said to be so sensitive that the color obtained with 1 part of nitrite in 750,000,000 parts of solution is visible when viewed through a 10-cm. column.

Determination of nitrite. Warington [3-5] used the Griess reaction for the determination of nitrite. In the original Griess-Warington method, the solution was acidified with hydrochloric acid, but Ilosvay [6-9] found that acetic acid should be used, since with this reagent color development is more rapid and there is a more uniform graduation of tint. Ilosvay further stated that the keeping qualities of the reagent are superior.

Weston [10] studied the effect of various factors upon the development of the color by the Griess-Warington method and the Ilosvay method, and found that an excess of hydrochloric acid interferes with the delicacy of the reaction, while an excess of acetic acid does not. Further, the speed of the reaction varies with the quantity of hydrochloric acid added, and is affected in some degree by an excess of the reagent. According to Weston, the Ilosvay method is more rapid than that used by Warington. In the Ilosvay method, the maximum color development does not occur until after several hours, but if the temperature and other conditions of the standard and sample are made the same, the color appears in each at the same rate, and may be compared after about 5 minutes. The determination is carried out as follows:

Reagents. *Sulfanilic acid reagent:* Dissolve 3.3 g. of sulfanilic acid in 750 ml. of water by heating and adding 250 ml. of glacial acetic acid.

a-Naphthylamine solution: Boil 0.5 g. of α-naphthylamine in 100 ml. of water for 5 minutes, filter through cotton, add 250 ml. of glacial acetic acid and dilute to 1 liter.

Procedure. Measure 100 ml. of water to be analyzed into a cylinder and add 10 ml. of the sulfanilic acid reagent. Then add 10 ml. of the α-naphthylamine solution. Mix well and compare after 10 minutes with standards similarly and simultaneously prepared. If the color developed in the sample is deeper than that of the standard, repeat the determination using separate portions of the sample properly and accurately diluted.

Standards for comparison are prepared as follows: Dissolve 0.4926 g. of pure sodium nitrite in water and dilute to 1 liter. Then dilute 100 ml. of this solution to 1 liter, and finally 10 ml. of the latter solution to 1 liter. One ml. of this solution contains 0.0001 mg. of nitrite nitrogen. To prepare a series of standards for comparison dilute 5, 10, 15 and 20-ml. portions of this solution to

100 ml. with nitrite-free distilled water. These standards correspond to 0.005, 0.01, 0.015 and 0.02 p.p.m. of nitrite.

If the water to be analyzed contains some color, it should be decolorized as follows: Transfer 200 ml. of the sample to a 250-ml. glass stoppered bottle and add 3 ml. of alumina cream and shake. Allow to stand for 15 minutes and filter. Discard the first 25 ml., and take 100 ml. of the remaining filtrate as the sample.[36,37]

Some salts such as sodium chloride accelerate the development of the color. Others have no influence, and still others such as borax retard color development. Certain organic compounds also retard the reaction, but this effect generally is overcome by the addition of a little sulfuric acid or sodium chloride.[38,39]

Acid fuchsin solutions are sometimes used as standards to eliminate the more tedious process of preparing nitrite solutions and developing the color in them.[40-42] These standards are prepared according to the method of Danet:[43,44]

Procedure. Dissolve 0.01 g. of fuchsin S in water and dilute to 1 liter. Use 3, 6, 9 and 12 ml. of this solution as standards. Place in comparison tubes and dilute to 100 ml. with water saturated with camphor to which 10 ml. of glacial acetic acid has been added for each liter. Seal the tubes with paraffin corks. These correspond to 0.005, 0.01, 0.015 and 0.02 p.p.m. of nitrite. Standards prepared in this manner must be checked against nitrite solutions because of the many possible sources of error.

Woodman and Norton[45] do not regard fuchsin standards as satisfactory.

Arney and Ring[46,47] have investigated permanent standards prepared from stable inorganic compounds. Richardson and Hollings[48] recommend reading the color in a Lovibond tintometer. Among others who have used α-naphthylamine for the detection of nitrites, the following references should also be listed.[49-58,86]

While applying the Griess-Ilosvay method to the determination of nitrite in soils and culture solutions, Sundara Rao[85] observed that the maximum tint was not obtained even after a period of two hours, and that the time taken for maximum color development varied widely. The only factor that appeared to affect the time required for this purpose was temperature. The following standardized method is suggested:

Procedure. Dilute a small aliquot of the original solution to 10 ml., and then add 1 ml. of the reagent mixture. Keep the mixture in a hot-water bath for 5 minutes. Cool under running water for 5 minutes, and take a reading with a one-half inch cell by comparing with glass tints.

Romijn[20-22] has modified the Griess reaction still further to prepare a reagent containing α-naphthylamine hydrochloride, sulfanilic acid, and tartaric acid. This reagent, which may be used for the determination of nitrite, is prepared as follows:

Reagent. Mix thoroughly 5 g. of α-naphthylamine hydrochloride, 445 g. of tartaric acid and 50 g. of sulfanilic acid. This reagent keeps indefinitely.

Standard nitrite solution. Dissolve 0.4926 g. of pure sodium nitrite in water and dilute to 1 liter. Dilute 10 ml. of this solution to 1 liter and mix thoroughly. One ml. of this solution contains 0.001 mg. of nitrogen.

Procedure. Place 50 ml. of the sample in a comparison tube and add a little of the reagent. When the color is developed, determine by duplication, dilution, or balancing. If the sample contains more than 0.15 mg. of nitrous acid per liter, the solution must be diluted and an aliquot used, since otherwise a precipitate will form. If the sample is very dilute, use 100 ml. for the analysis.

To prepare a standard for the balancing or dilution method, dilute 1 ml. of the nitrite standard with 800-900 ml. of water and add 1 ml. of the reagent. Dilute to 1 liter and mix thoroughly. One ml. of this standard contains 0.0001 mg. of nitrogen.

Romijn[20] has also used a reagent consisting of 1 part of α-naphthylamine, 10 parts of sulfanilic acid and 10 parts of tartaric acid. Kolthoff[23,24] claims that this reagent is very easily affected by such factors as time, temperature and concentration.

Meerburg[21,22] has used this reaction, and has recommended the addition of sodium chloride to hasten color formation. Bicarbonates retard the reaction, and should be neutralized before adding sodium chloride.

The blue-violet dye formed by coupling diazotized α-naphthylamine with β-naphthylamine-6,8-disulfonic acid in an acid solution is suitable for the colorimetric determination of nitrite. When this method is used, both sample and standard must be of nearly the same concentraton or the character of the color is so altered that sample and standard cannot be compared. A red color is obtained when the concentration of nitrite exceeds 0.07 mg. of nitrite per ml.

The following procedure is used for the determination of nitrite in blood.[28,29]

Reagents. *α-Naphthylamine solution:* Boil about 0.1 g. of α-naphthylamine with 20 ml. of water and decant the colorless solution. This is used as the reagent.

α-Naphthylamine-6,8-disulfonic acid: Add a small drop of commercial 32.6 per cent solution of the sodium salt of amino-*G* acid to 50 ml. of water. Add about 10 ml. of glacial acetic acid to obtain a colorless or faint pink solution.

Standard nitrite solution: Dissolve 0.0200 g. of sodium nitrite in water and dilute to 1 liter. One ml. of this solution contains 0.0134 mg. of nitrite radical. When ready to use, dilute as required.

Procedure. Add exactly 8 ml. of freshly drawn blood to 20 ml. of a solution containing 4.5 per cent of zinc sulfate heptahydrate. The blood should be added quickly to prevent loss of nitrite. Mix thoroughly and add 4 ml. of N sodium hydroxide solution with thorough mixing. Centrifuge, but do not filter, since a loss of nitrite occurs with filtration.

Mix 8 ml. of the clear centrifugate with 8 ml. of the α-naphthylamine reagent and 8 ml. of the α-naphthylamine-6,8-disulfonic acid. Simultaneously treat a similar volume of the standard in the same way. Heat both sample and standard in a water-bath at 80° C. to develop the maximum color. This requires about 20 minutes, and no fading occurs within about 18 hours.

An artificial standard may be prepared by dissolving 0.0937 g. of potassium permanganate in water and diluting to 1 liter. The color of this solution is equivalent to that derived from 0.01 mg. of sodium nitrite or 0.00667 mg. of the nitrite radical.

Determination of potassium. Potassium is determined indirectly after precipitating as potassium sodium cobaltinitrite, $K_2Na[Co(NO_2)_6] \cdot H_2O$, by estimating the quantity of nitrite present in the precipitate after developing with α-naphthylamine and sulfanilic acid. Potassium is precipitated in the usual manner, and the nitrite is then determined as follows:[59-61]

Reagent. Boil 1 g. of α-naphthylamine with 100 ml. of water and add 750 ml. of 10 per cent acetic acid. Mix this solution with a second solution prepared by dissolving 2.5 g. of sulfanilic acid in 750 ml. of 10 per cent acetic acid. This reagent should be colorless, and may be stored for some time in a dark bottle.

Procedure. Precipitate potassium from the unknown solution with sodium cobaltinitrite, and at the same time prepare a standard precipitate by the same treatment, using a solution of known potassium content. Add 5 ml. of the reagent to each of the cobaltinitrite precipitates and heat the mixtures for 2 minutes in boiling water. Transfer the resulting red solutions to 100-ml. flasks and again treat the residues with an additional 5 ml. of the reagent. Repeat the treatment as long as any residue remains. Cool the solution and dilute to the mark with cold α-naphthylamine reagent and compare the resulting colors.

Determination of sodium. Sodium may be separated from potassium and other metals with which it is usually associated by precipitating as the complex sodium cesium bismuth nitrite, $6NaNO_2 \cdot 9CsNO_2 \cdot 5Bi(NO_2)_3$.[62] This compound may be dissolved and the sodium determined indirectly by comparison of the bright red color produced by the nitrite with α-naphthylamine and sulfanilic acid.[63] The chloride concentration of the unknown solution should not exceed 0.2 N since otherwise bismuthoxychloride may separate. Phosphates, if present in more than traces, should be removed. Iodide, citrate and many of the heavy metals, especially iron and silver, interfere and should be removed.

Reagent. *Bismuth cesium nitrite solution:* Dissolve 30 g. of sodium-free potassium nitrite in 60 ml. of water and add 3 g. of bismuth nitrate dissolved in 5 ml. of 2 N nitric acid. If a precipitate forms, clear the solution by carefully adding 1:1 nitric acid. Add 16 ml. of a 10 per cent solution of cesium nitrate. Dilute the mixture to 100 ml. and again add nitric acid if a turbidity appears. The reagent should have a clear orange-yellow color. Cool the mixture to 1° C. and allow to stand for 24 hours, and then filter off any sodium salts which may be present. The reagent may be stored under illuminating gas and at a temperature of 1° C. for several weeks.

Procedure. Cool the solution containing sodium to 10-12° C. and add 3 ml. of the bismuth cesium nitrite solution for each mg. of sodium present. Fit the flask with a two-hole rubber stopper which contains 2 glass tubes bent at right angles. Attach to one of the tubes a short piece of rubber tubing fitted with a glass plug and equip the other with a Bunsen valve and plug. Remove the plugs and pass illuminating gas which has been freed from hydrogen sulfide into the flask for a few seconds, and then replace the plugs. Allow the flask to stand at 1° C. for 24 hours to facilitate the formation of the yellow crystalline precipitate.

Filter rapidly through a Gooch crucible and wash quickly with five 2-ml. portions of ice-cold 50 per cent acetone solution that is saturated with sodium cesium bismuth nitrite. Transfer the precipitate to a beaker and warm with 10 ml. of a mixture containing equal parts of 10 per cent potassium hydroxide solution and 10 per cent tartaric acid solution. Transfer to a 100-ml. graduated flask and cool. Dilute to the mark and mix thoroughly. Measure an aliquot containing approximately 0.01 mg. of sodium into a second 100-ml. graduated flask. Place 1 ml. of the standard nitrite solution in a similar flask and dilute both to about 90 ml. To each add 2 ml. of 0.8 per cent solution of sulfanilic acid in 5 N acetic acid and 2 ml. of a 0.5 per cent solution of α-naphthylamine in 5 N acetic acid. Dilute both solutions to 100 ml. and mix thoroughly. Allow to stand for 20 minutes and compare the resulting colors.

This method is accurate to about 5 per cent. The standard nitrite solution is prepared by dissolving 0.0300 g. of pure sodium nitrite in water and diluting to 1 liter. One ml. of this solution contains a quantity of nitrite equivalent to 0.01 mg. of sodium.

Detection of ammonia. Diazotized α-naphthylamine reacts with ammonia to give a colored compound that may be used for the detection of the latter. A test paper is prepared by impregnating paper with a solution obtained by treating α-naphthylamine with sodium nitrite and hydrochloric acid. With this reagent it is possible to detect a small fraction of a milligram of ammonia in 1 liter of air.[64]

Detection and determination of nitrate. Nitrates are detected and determined by a procedure which is based upon the reduction of nitrates, and the color reaction obtained with the resulting nitrite when treated with α-naphtylamine and sulfanilic acid.[65-70] This method is illustrated by the following procedure:[70]

Reagents. *Sulfanilic acid solution:* Mix 10.5 g. of sulfanilic acid, 6.8 g. of sodium acetate, 300 g. of acetic acid and 600 ml. of water and heat to boiling for 3 minutes. Cool and dilute to 1 liter.

a-Naphthylamine solution: Heat a little more than 1 liter of water to boiling and mix with 5 g. α-naphthylamine. Boil 5 minutes and filter, and to a little less than 1 liter of the hot filtrate add 5 ml. of concentrated hydrochloric acid. Cool and dilute to 1 liter.

Iodine solution: Dissolve 1.3 g. of iodine in 100 ml. of glacial acetic acid.

Sodium thiosulfate solution: Dissolve 2.5 g. of sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$, in 100 ml. of water.

Procedure. To 10 ml. of the solution to be analyzed, having a pH of 2-3.5, add 1 g. of ammonium sulfate and dilute with water to 20 ml. Cool to 0° C. and add 1 g. of zinc. Keep the temperature at 0° C. for 3 minutes, and then remove the zinc. To 10 ml. of the resulting mixture, add 1 ml. of sulfanilic acid solution and 1 ml. of a solution of iodine in acetic acid. After exactly 3 minutes remove the iodine with sodium thiosulfate, add 1 ml. of α-naphthylamine and dilute to 50 ml. Compare the resulting color with that of solutions of sodium nitrate similarly treated.

If the color developed in this procedure is too intense, a smaller portion of the original solution should be used. Copper and iron salts interfere and must be absent. For a solution containing 0.14-1.4 mg. of nitrate nitrogen per liter, the accuracy of this method is 3 per cent.

When 1 ml. of a solution to be tested and 1 ml. of a saturated aqueous solution of α-naphthylamine are stratified on concentrated sulfuric acid, a violet-red ring forms if nitrate is present. This test is given with as little as 0.025 mg. of potassium nitrate. Other oxidizing agents do not interfere.[71]

Detection and determination of chromium. A solution containing 0.5 g. of α-naphthylamine and 50 g. of tartaric acid in 100 ml. of water is colored blue by the addition of a solution containing as little as 0.1 mg. of chromic acid in 100 ml. of water.[72,73] This reaction may be used for the colorimetric determination of chromium by comparing the color of the unknown with that of a standard chromium solution.

Detection and determination of gold. α-Naphthylamine reacts with gold chloride to form a blue or reddish-violet precipitate which may be used for the detection of gold. The gold precipitate contains 47.8 per cent gold. The reaction is sensitive to 0.001 mg. of gold in 100 ml. of water.[74] Gold is determined colorimetrically by the method of Paulsen and Pevzner:[75]

Procedure. Dilute 1 ml. of solution to be analyzed to 10 ml. with water and add 1 ml. of 0.1 per cent α-naphthylamine solution. Compare the resulting violet color with that of a standard similarly treated.

The color of the solution increases for 2-3 minutes and then remains the same for about 1-2 hours. High results are obtained if the solution is allowed to stand longer than 2 hours. The intensity of the color obeys Beer's law. As much as 0.1 per cent copper, zinc, lead and iron do not interfere, although palladium must be absent. The accuracy of the method is said to ±2 per cent.

The determination of gold cannot be carried out in a strongly acid solution, because of the formation of decomposition products. In an alkaline solution a blue color is obtained which is not stable. Acidifying an alkaline solution causes the formation of sodium chloride or other salt, and this decreases the stability of the color to such an extent that the determination is not possible. For these reasons the use of α-naphthylamine does not appear to be very satisfactory for the gold determination.[76]

Determination of tungsten. When α-naphthylamine is added to a solution of sodium tungstate, a precipitate is formed which corresponds in composition to $2(C_{10}H_9N) \cdot 5WO_3 \cdot 3H_2O$. Since precipitation is quantitative, this reaction is used for the determination of tungsten:[77]

Reagent. Dissolve 25 g. of α-naphthylamine and 22 ml. of concentrated hydrochloric acid in a liter of water.

Procedure. To 100 ml. of the reagent solution, slowly add from a buret 25 ml. of the solution to be analyzed, which should contain not more than 20 g. of WO_3 per liter. The tungstate solution should be added slowly at ordinary temperature to the slightly acidified α-naphthylamine solution. Allow the mixture to stand for 3 hours and filter. Wash the precipitate with a 1:5 solution of the precipitant and ignite to WO_3 in an inclined platinum crucible.

Detection of thallium. Alcoholic solutions of thallic salts produce a violet color or precipitate with α-naphthylamine. This reaction has been recommended by Renz [78] for the differentiation of α- from β-naphthylamine, although it may be used for the detection of thallium salts.

Detection and determination of mercury and copper. Copper and mercury are detected by the formation of complex metal thiocyanates with α-naphthylamine.[79] The mercury complex is prepared as follows:

Procedure. To an aqueous solution of mercuric chloride, containing about 0.5 per cent mercury, add 4-5 ml. of 2 N potassium thiocyanate and 3-4 drops of a 4 per cent alcoholic solution of α-naphthylamine. A yellow crystalline precipitate forms slowly. The precipitate does not form in the presence of an excess of potassium thiocyanate. The limits in the concentration of the reagents used are 0.5-20 ml. of potassium thiocyanate solution for each 10 ml. of mercuric chloride solution and 0.2-0.5 ml. of α-naphthylamine solution. The precipitate dissolves on heating but reappears on cooling.

The mercury precipitate does not form in an acid or alkaline medium. The precipitate is $Hg(C_{10}H_7NH_2)_2(SCN)_2$. This reaction is sensitive to 1 part of mercury in 27,000 parts of solution. If a few drops of 2 N potassium thiocyanate solution and 3 or 4 drops of alcoholic α-naphthylamine solution are added to a neutral solution of a cupric salt, a blue-violet precipitate forms which changes to blue on boiling. Very dilute solutions yield only a blue color. The precipitate is insoluble in potassium thiocyanate. This reaction is sensitive to 1:300,000. The reaction with copper has been explained as an induced reaction in which the thiocyanate oxidizes α-naphthylamine.[80] Precipitation of both copper and mercury is quantitative and consequently the above reactions may be used for the gravimetric determination of these metals.

Determination of iodine. Iodine oxidizes hydroxylamine to nitrous acid,

$$NH_2OH + 2I_2 + H_2O \rightarrow HNO_2 + 4HI$$

which in turn may be made to react with sulfanilic acid to form a diazonium salt. This compound may be coupled with α-naphthylamine to form a red dye which may be estimated colorimetrically. This reaction has been used by Endies and Kaufmann [81] for the determination of iodine and iodides.

Iodides are first oxidized to iodates with bromine water and iodine is liberated by the addition of potassium iodide. The mixture is then distilled and the iodine in the distillate is determined by a method based upon the above reactions. As little as 5γ of iodine or 1γ of iodide may be determined by this method with an accuracy of 2 per cent.

Detection of oxygen. Oxygen is detected by a reaction which is based upon the fact that a piece of filter paper moistened with a little α-naphthylamine in dilute acetic acid is colored red when treated with nitric oxide in the presence of oxygen.[82] Sheaff [83] used a similar procedure for the determination of small quantities of oxygen. Nitrite is formed by the interaction of oxygen and nitric oxide in a solution containing sodium hydroxide, and the nitrite is then estimated colorimetrically after treating with α-naphthylamine and sulfanilic acid. This method is sensitive to 0.0001 mg. of oxygen.

Detection of ozone. Van Eck [84] has used α-naphthylamine and tartaric acid as a reagent for ozone.

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β-NAPHTHYLAMINE

Synonym: 2-Aminonaphthalene

$C_{10}H_9N$ Mol. Wt. 143.18 Beil. Ref. XII, 1265.

$$C_{10}H_7—NH_2$$

Use: Detection of ammonia, cadmium, cobalt, copper, gold, manganese, mercury, platinum and thallium.

Determination of nitrite.

β-Naphthylamine consists of white to reddish crystals which are volatile in steam. It melts at 111-113° C., and boils at 306° C. It is soluble in hot water, alcohol and ether.

Preparation: Mix intimately 1 part of β-naphthol and 4 parts of calcium chloride-ammonia. This material is prepared by passing dry ammonia gas over anhydrous calcium chloride. By using powdered calcium chloride and treating for 12 hours with ammonia, a product is obtained which contains 47 per cent ammonia. Heat the mixture of β-naphthol and calcium chloride-ammonia in a closed tube for 8 hours at 260-270° C. Open the tube and warm the contents with hydrochloric acid and filter. Mix the filtrate with an excess of ammonium hydroxide and extract with ether. Separate the two layers, and treat the ether layer with sodium hydroxide to remove the excess β-naphthol, and again separate. Remove most of the ether by distillation, and recrystallize the impure product by dissolving in water and allowing to cool.[1]

Bucherer[18] uses the following method:

Mix thoroughly 100 g. of β-naphthol with 150 ml. of a 40 per cent solution of ammonium sulfite and 100 ml. of 20 per cent aqueous ammonia. Place the mixture in a 500-ml. autoclave, and allow to react at a temperature of 100-150° C. The reaction is completed when the quantity of β-naphthol no longer decreases. Extract the crude product with a dilute solution of sodium hydroxide to remove small amounts of β-naphthol. Dissolve the residue in dilute hydrochloric acid, and filter from any β-dinaphthylamine which may have been formed. Precipitate the base from the filtrate by the addition of sodium hydroxide.

Reactions with metal salts. From time to time various investigators have reported compounds which are obtained by the reaction of β-naphthylamine with metallic salts. These compounds are coordination complexes similar to those formed with ammonia. Compounds which have been prepared and reported are listed in Table 46.

Detwiler and Willard[12,17] have studied the reactions of β-naphthylamine with a number of metallic salts, and suggest that β-naphthylamine might be used to detect gold, mercury, platinum, cobalt, manganese, copper, cadmium and ammonia. Pure β-naphthylamine, which is used for the precipitation of metal salts, is best prepared in small quantities by repeated sublimation of the raw material. β-Naphthylamine hydrochloride is a more satisfactory reagent than the pure amine.

TABLE 46.—COMPOUNDS OF β-NAPHTHYLAMINE WITH METAL SALTS
($B = C_{10}H_7NH_2$)

Compound	Description	Reference
$PtCl_4 \cdot 2B$	leaflets	2
$PtCl_4 \cdot 2B \cdot 2HCl$		2
$Pt(SCN)_4 \cdot 2B \cdot 2HSCN$	yellow crystals	3
$PdCl_2 \cdot 2B$		4
$PdCl_2 \cdot 2B \cdot HCl$	yellow leaflets	4
$PdBr_2 \cdot 2B$	yellow	4
$PdBr_2 \cdot 2B \cdot HBr$	dark red leaflets	4
$CuCl_2 \cdot 4B$		5
$CuSO_4 \cdot 2B$	red amorphous	6
$Cu(NO_3)_2 \cdot 2B$	green-brown crystals	7
$AgNO_3 \cdot 2B$	needles	5
$Ni(SCN)_2 \cdot 2B$	yellow-green crystals	10
$TeBr_4 \cdot 2B$	yellow-orange amorphous	11
$ThCl_4 \cdot B$	gray-white	7
$TlCl_3 \cdot 3B$	silvery leaflets	8
$PbCl_4 \cdot B$	dark green	7
$ZrCl_4 \cdot 2B$	gray-brown	7
$2HgCl_2 \cdot 3B$	yellow crystals	5
$H_3Fe(CN)_6 \cdot 3B \cdot H_2O$	gray white plates	
$H_4Fe(CN)_6 \cdot 4B \cdot H_2O$	white needles	

When an alcoholic solution of β-naphthylamine and cadmium nitrate are mixed and the solution allowed to evaporate, beautiful dark brown fern-like crystals appear. Green plates and rods are obtained when a mixture of an alcoholic solution of β-naphthylamine and copper nitrate is evaporated. When β-naphthylamine hydrochloride is added to acid solutions of ferric chloride, palladous chloride and lithium chloride, precipitates form immediately. The iron precipitate is grayish-green and amorphous; the palladium precipitate is light brown; and the lithium precipitate is milky and amorphous. Crystalline precipitates are also obtained when β-naphthylamine hydrochloride is added to acid solutions of various metallic salts, and the resulting mixtures are allowed to evaporate slowly. Beautiful vitreous dark purple crystals are obtained with gold chloride; silvery, mica-like plates are formed with mercuric chloride; and yellow rods and needles are obtained when β-naphthylamine hydrochloride is added to an alcoholic solution of platinum chloride. Cream to white rosettes are formed when ammonium choride is added to β-naphthylamine. Gray dendrites, which are green when wet, are formed when a solution of cobalt chloride is added to β-naphthylamine.

β-Naphthylamine and manganese chloride in an acid solution yield brown needles and leaflets. Dubsky and coworkers[13] report that this reaction is not sufficiently sensitive to be of much value for the detection of manganese.

Thallic salts in alcoholic solution produce a crystalline compound having a silvery luster when treated with β-naphthylamine. A hydrochloric acid solution of thallic chloride and β-naphthylamine, also in a hydrochloric acid solution, yields $TlCl_3(C_{10}H_7NH_2 \cdot HCl)_3$.[8]

A precipitate of $[Cu(C_{10}H_7NH_2)_2]SO_4$ is obtained when a concentrated alcoholic solution of β-naphthylamine and a solution of a copper salt are added to an alcoholic solution containing sodium sulfate. This reaction has been used by Spacu[14] for the microchemical detection of copper:

Procedure. To an alcoholic solution of sodium sulfate add 2 drops of a concentrated alcoholic solution of β-naphthylamine and a small drop of the copper solution. If copper is present, a characteristic precipitate is obtained.

Acids and bases and alkali halides interfere with this reaction. The presence of thiocyanates makes the reaction somewhat more sensitive. Mercury, silver, bismuth, lead, cadmium, tin, antimony, arsenic, nickel, cobalt, zinc, aluminum, manganese, chromium, calcium, strontium, barium, sodium, and potassium do not interfere. Iron, however, must be absent while making the test.

Detection of ammonia. Korenman[15] has used β-naphthylamine in a sensitive test for detecting ammonia in air. The test is carried out by diazotizing β-naphthylamine with sodium nitrite and hydrochloric acid, and impregnating a strip of filter paper with this solution. The prepared paper is pale greenish-yellow in color, but in the presence of ammonia the color changes to a dark orange-brown. By means of this reaction it is possible to detect as little as 0.018 mg. of ammonia in 1 liter of air.

Determination of nitrite. β-Naphthylamine is used with sulfanilic acid in place of the α-isomer in the well-known Griess reaction for nitrites. Koehler and Marqueyrol[16] used this reagent for the determination of nitrite in nitrocellulose.

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2-NAPHTHYLAMINE-5-SULFONIC ACID Synonym: Dahl's Acid

$C_{10}H_9O_3NS$ Mol. Wt. 223.24 Beil. Ref. XIV, 748(733).

$$HO_3S—C_{10}H_6—NH_2$$

Use: Detection of nitrite.

2-Naphthylamine-5-sulfonic acid is obtained along with other isomers by the sulfonation of β-naphthylamine. It is a white crystalline solid which is almost insoluble in water and in alcohol.

Detection of nitrite. 2-Naphthylamine-5-sulfonic acid has been used as a coupling agent for diazotized dyes.[1]

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[1] J. V. Dubsky and A. Okac, *Z. anal. Chem.* 75, 92 (1928).

N-(1-NAPHTHYL) ETHYLENEDIAMINE DIHYDROCHLORIDE

$C_{12}H_{14}N_2 \cdot 2HCl$ Mol. Wt. 259.15 Beil. Ref. XII, 1251.

$$C_{10}H_7—NH—CH_2—CH_2—NH_2 \cdot 2HCl$$

Use: Determination of nitrite, potassium and sulfate.

N-(1-naphthyl) ethylenediamine dihydrochloride is a greenish-yellow to golden-yellow crystalline solid. It melts at 165.3-165.7° C. It is fairly soluble in alcohol but is only slightly soluble in ether and moderately soluble in benzene. It is soluble in glacial acetic acid.

Preparation: Mix 20 g. of α-naphthylamine with 20 g. of bromoethylphthalimide and heat to 160° C. on a water-bath. Wash the thick product with a considerable quantity of water and then with hot alcohol. Crystallize the yellow product which remains, and grind intimately with an equal weight of solid sodium hydroxide. Distill the mixture rapidly at 10-20 mm. pressure. Discontinue the distillation when the residue begins to char at 340° C. Extract the distillate with the calculated quantity of 0.05 N hydrochloric acid and decolorize with charcoal. Treat the solution with sodium hydroxide to liberate the base, and extract with benzene. Dry the benzene extract over solid sodium hydroxide, and remove the solvent by distillation. Dissolve the base in a little alcohol and add the calculated quantity of hot alcoholic picric acid. Allow to cool and recrystallize the picrate from 6 N acetic acid. Suspend the picrate in warm water and treat with an excess of sodium hydroxide. Extract the base with benzene and dry over solid sodium hydroxide. Finally prepare the dihydrochloride by bubbling dry hydrogen chloride into the benzene solution.[1]

Bratton and Marshall[2] have used a method similar to that described above, except that 2.5 moles of α-naphthylamine to 1 mole of β-bromoethylphthalimide were used, and the product was recrysallized from glacial acetic acid.

Determination of nitrite. Many procedures have been proposed for the colorimetric determination of nitrite in water, foods, and other materials which have been based upon the diazotization of sulfanilic acid by nitrous acid, and the subsequent coupling of the diazo compound with some such substance as α-naphthylamine. According to Shinn[3] these methods are open to the following criticisms: (a) the coupling of diazotized sulfanilic acid with α-naphthylamine is relatively slow and requires 10-30 minutes for full color development;[4] (b) with α-naphthylamine acetate as the coupling agent, the color must be read within 30 minutes;[5] and (c) the primary nitrite standards are unstable and difficult to prepare.

These difficulties may be eliminated by replacing α-naphthylamine with N-(1-naphthyl)ethylenediamine dihydrochloride. This reagent has been used by Bratton and Marshall[2] for the determination of sulfanilamide. This amine is water soluble, and decreases the time required for color development to two minutes, and gives a final color that remains constant for several hours. It is also less sensitive to variation in acidity and reacts equally well in acid concentrations ranging from 0.1 to 1.0 N. Shinn[3] has also suggested replacing sulfanilic acid with sulfanilamide in the nitrite determination. The latter may be obtained in a high state of purity; it is more stable than sulfanilic acid, both in solution and in the solid state; and it couples more rapidly than sulfanilic acid.

Since the methods for the colorimetric determination of nitrite and sulfanilamide[2,6] use the same fundamental reactions of diazotization and coupling, and since the concentrations analyzed are similar, the substitution of a standardized stock solution of sulfanilamide for the primary nitrite standard has been proposed. Experiments have shown that sulfanilamide and nitrite react stoichiometrically in the presence of a suitable excess of either reagent.

For the details of the procedure, see section on sulfanilamide

Kershaw and Chamberlin[8] have studied the method of Shinn[3] to determine its applicability to the estimation of nitrites in water. The method as published is not suitable to waterworks practice, because of lack of sensitivity in the range from 0.001 to 0.015 p.p.m. nitrite nitrogen. The method may, however, be made applicable by certain modifications.

Determination of potassium. Potassium may be determined in blood serum by precipitating as potassium cobaltinitrite and determining the nitrite content of the precipitate. N-(1-naphthyl)ethylenediamine dihydrochloride and sulfanilamide have been used for this purpose.[7] This reaction is sensitive to 0.002 mg. of potassium per 100 ml.

Determination of sulfate. Klein[9] recommends the following method for the determination of small quantities of sulfate: Precipitate sulfate in the sample as benzidine sulfate, purify, and dissolve in 0.2 N hydrochloric acid. Diazotize the amine, destroy the excess nitrous acid, and couple the diazo compound with N-(1-naphthyl)ethylenediamine dihydrochloride, and then read the intense purple color in a Klett-Summerson photoelectric colorimeter.

This method offers many advantages over others which have been used. The method is simple to carry out, and the color is remarkably stable. It shows no decrease after 12 hours, and follows Beer's law closely. For limitations of the benzidine sulfate precipitation in the presence of large quantities of chloride and phosphate, see section on benzidine (page 302).

Reagents. *N-(1-naphthyl)ethylenediamine dihydrochloride solution:* Prepare a 0.1 per cent solution of the reagent in distilled water. Store in a dark bottle.

Benzidine hydrochloride reagent: Dissolve 4.0 g. of benzidine hydrochloride in a small quantity of distilled water and dilute to 250 ml. with 0.2 N hydrochloric acid.

Standard benzidine hydrochloride solution: Dissolve 0.4014 g. of pure benzidine hydrochloride in a small quantity of 0.2 N hydrochloric acid, and dilute to 100 ml. with the same acid. 1.0 ml. of this solution is equivalent to 1.5 mg. of sulfate. The standard is prepared by diluting 1.0 ml. of the above solution to 100 ml. with 0.2 N hydrochloric acid. 1.0 ml. of this solution is equivalent to 0.015 mg. of sulfate.

Standard sulfate solution: Dissolve 0.5437 g. of pure potassium sulfate in distilled water and dilute to 1 liter. 1.0 ml. of this solution is equivalent to 0.3 mg. of sulfate. Prepare the standard by diluting 10 ml. of the above solution to 100 ml. with distilled water. 1.0 ml. of this solution is equivalent to 0.03 mg. of sulfate.

Procedure. Place 1.0 ml. of glacial acetic acid and 1.0 ml. of the benzidine hydrochloride reagent in a 15-ml. centrifuge tube, and add a quantity of the sample solution containing between 0.015 and 0.15 mg. of sulfate. Mix, and add 2.0 ml. of 1:1 acetone-ethyl alcohol mixture. Cap the tube and mix its contents thoroughly by rolling between the hands. Allow the tube to stand in ice-water for one-half hour to complete precipitation.

Centrifuge 10 minutes at 2500 r.p.m. Pour off the supernatant liquid by inverting the tube, and while still inverted, touch the mouth of the tube to a piece of filter paper to remove the excess liquid. Allow to drain on the filter paper for 5 minutes.

Wash the walls of the tube with 2.0 ml. of the 1:1 acetone-ethyl alcohol mixture, but avoid disturbing the precipitate. Centrifuge for 5 minutes, pour off the supernatant liquid, and allow to drain 5 minutes on filter paper as before. Repeat the washing and draining procedure.

Add 2.0 ml. of 0.2 N hydrochloric acid to the centrifuge tube to dissolve the precipitate. Place the tube in ice-water, and add 1.0 ml. of a freshly prepared 0.1 per cent solution of sodium nitrite. Shake and allow to stand 3 minutes. Then add 1.0 ml. of 0.5 per cent ammonium sulfamate solution. Again shake, and allow to stand an additional 2 minutes. Finally, add 1.0 ml. of the *N*-(1-naphthyl)ethylenediamine dihydrochloride solution to develop the color. Mix and allow the solution to stand 20 minutes. Transfer quantitatively to a 50-ml. volumetric flask, and dilute to the mark with distilled water. Measure in a photoelectric colorimeter, using a green filter. The Klett No. 54 is satisfactory if the Klett-Summerson instrument is used.

Either the standard benzidine hydrochloride or the standard sulfate solution containing 0.03 mg. of sulfate may be used for the comparison. These should be run at the same time as the unknown. The benzidine solution need only be diazotized and coupled, while the sulfate solution must be carried through the entire procedure described above. A blank, using 2.0 ml. of 0.2 N hydrochloric acid, diazotized and coupled with the color reagent, serves as zero reading on the photometer.

The amount of sulfate present is calculated from the following expression:

$$\frac{\text{Reading of unknown}}{\text{Reading of standard}} \times \text{concentration of standard} = \text{mg. of } SO_4 \text{ in sample}$$

This method is accurate in the range extending from 0.05 to 0.15 mg. of sulfate with a maximum error of 2 per cent. Results obtained using pure sulfate solutions are summarized in Table 47.

TABLE 47.—DETERMINATION OF SULFATE

Sulfate Present mg.	Sulfate Found mg.	Error mg.	Error Per Cent
0.015	0.0152	0.0002	1.3
0.030	0.0300	0.0000	0.0
0.030	0.0303	0.0003	1.0
0.060	0.060	0.0000	0.0
0.060	0.0597	0.0003	0.5
0.090	0.0921	0.0021	2.3
0.150	0.1470	0.0030	2.0

1. H. E. Newman, *Ber.* 24, 2199 (1891).
2. A. C. Bratton and E. K. Marshall, Jr., *J. Biol. Chem.* 128, 537 (1939).
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7. J. M. Looney and C. G. Dyer, *J. Lab. Clin. Med.* 28, 355 (1942); *C.A.* 37, 6688 (1943).
8. N. F. Kershaw and N. S. Chamberlin, *Ind. Eng. Chem,, Anal. Ed.* 14, 312-13 (1942).
9. B. Klein, *Ind. Eng. Chem., Anal. Ed.* 16, 536-37 (1944); *C.A.* 38, 5751 (1944).

β-NAPHTHYLPHENYLAMINE Synonym: Phenyl-β-naphthylamine

$C_{16}H_{13}N$ Mol. Wt. 219.27 Beil. Ref. XII, 1275(535).

$C_6H_5—NH—C_{10}H_7$

Use: Detection of chlorate.

β-Naphthylphenylamine is a crystalline solid melting at 107.5-108° C. It boils at 395-395.5° C. It is moderately soluble in cold alcohol, ether, benzene and acetic acid.

Preparation: Mix 10 g. of freshly distilled anhydrous aniline with 15 g. of finely powdered β-naphthol and 11.6 g. of calcium chloride in a closed tube and heat for 9 hours at 220-230° C. Remove the calcium chloride and unchanged aniline by treating with boiling water that has been acidified with hydrochloric acid. A brown oil collects on the bottom of the vessel and this is freed from the supernatant liquid by decantation. On washing and cooling, the oil solidifies to a brown crystalline mass. This is freed of unchanged β-naphthol by extraction by continuous boiling with sodium hydroxide. Wash, dry, and heat until melted, and then allow to cool. The compound obtained is a dark crystalline mass.[1]

The reagent is also prepared by the following method described by Graebe:[2]

Heat 90 g. of β-naphthol and 112.5 g. of aniline for 7 hours at 100-190° C. with 1 g. of iodine. Boil the melt, first with dilute hydrochloric acid, and then with dilute sodium hydroxide. Dry the residue and distill *in vacuo*. The reagent distills at 237° C. at 15 mm. Recrystallize from methyl alcohol.

Detection of chlorate. β-Naphthylphenylamine reacts with various oxidizing agents to give color reactions which may be used for the detection of these substances. Thus for example, β-naphthylphenylamine reacts with nitrates to give a green coloration; with nitrite to give an emerald-green color; and with chlorate to give a clear red to violet color.[3]

Chlorates react somewhat differently from the various other oxidizing agents to give a red coloration. For this reason β-naphthylphenylamine dissolved in concentrated sulfuric acid constitutes a fairly specific reagent for chlorate and makes possible the detection of small quantities of this ion. The following procedure is recommended by Sa[3] for the detection of small quantities of chlorates:

Procedure. Place 2 ml. of a 0.01 per cent solution of β-naphthylphenylamine in concentrated sulfuric acid in a test tube and cool by immersing in a beaker filled with ice water. Then add dropwise from a pipet 0.5 ml. of the solution to be tested, which contains about 0.1 mg. of chlorate per ml. of solution.

The sensitivity of this reaction is increased by using the following procedure: Place 1 ml. of a 0.001 per cent solution of the reagent in concentrated sulfuric acid in a small test tube and overlay with 0.2 ml. of the solution to be tested. Upon agitating the tube and contents lightly a red or pale violet color is observed in the aqueous layer. In this way as little as 0.01 mg. per ml. of chlorate can be detected.

The quantity of the chlorate used, and the concentration of the amine are rather important in carrying out this test. In the presence of an excess of chlorate the color may be yellow or yellowish-red, according to the concentration, while an excess of the reagent diminishes the sensitivity of the test. If the chlorate is added to the sulfuric acid solution without cooling, the color becomes violet-brown, but if warming of the solution is prevented by cooling in ice water, the color is pure and stable. The presence of considerable quantities of chloride, bromide and iodide may interfere with the above reaction. Nevertheless, the color is perfectly clear and there is no variation in its tint if for one part of chlorate the proportion of chloride or bromide does not exceed one, or for iodide, 0.1. Perchlorates do not interfere.

Tests made with solutions of other oxidizing agents of the same concentration as that of the chlorate have shown that the reaction is different from that of numerous other substances, such as bromate, iodate, perchlorate, periodate, nitrate, nitrite, permanganate, ferricyanide, ferrocyanide, vanadate, chromate, dichromate, tungstate, arsenate, persulfate, molybdate, hydrogen peroxide, mercuric and cupric ions and bromine.

1. E. Friedlander, *Ber.* **16**, 2076-77 (1883).
2. C. Graebe, *Ber.* **13**, 1850 (1880).
3. H. Sa, *Anales farm. bioquim.* **5**, 111-4 (1934) ; *C.A.* **30**, 6672 (1936).

o-NITROANILINE

$C_6H_6O_2N_2$ Mol. Wt. 138.12 Beil. Ref. XII, 687.

$$O_2N—C_6H_4—NH_2$$

Use: Detection of iodide.

o-Nitroaniline is an orange-yellow crystalline solid. It melts at 71-72° C. It is slightly soluble in cold water, soluble in hot water, and readily soluble in alcohol and chloroform.

Preparation: Suspend 45 g. of finely powdered acetanilide in 50 g. of acetic anhydride, which has been cooled to about 5° C., and stir with the aid of a mechanical stirrer. Cool 25 ml. of fuming nitric acid ($d = 1.5$) in ice and mix with 0.5 g. of urea and 15 g. of acetic anhydride. Pour the cooled acid mixture slowly into the acetanilide suspension, keeping the temperature below 10-20° C. Allow the mixture to stand overnight, and then mix with 500 g. of crushed ice. Filter off the yellow crystals of the mixture of *o*- and *p*-nitroacetanilide, wash with water, and dry.

Separate the two isomers as follows: Place in a beaker 400 ml. of a solution prepared by adding 1 volume of ethyl alcohol and 4 volumes of water to 1 volume of a 50 per cent aqueous solution of potassium hydroxide. Cool in ice to 0° C. and stir. Add gradually with stirring the powdered mixture of the two isomers and continue the stirring for 2 or 3 hours. The *o*- compound dissolves and its solution is filtered from the *p*- derivative. Wash first with about 60 ml. of the same potassium hydroxide solution, which is also cooled with ice, and finally with ice-water. On standing the large needle-shaped crystals of *o*-nitroacetanilide separate from the red solution. Filter and wash with water and finally recrystallize from ethyl alcohol.

Heat the *o*-nitroacetanilide with concentrated hydrochloric acid, or with a mixture of equal volumes of concentrated sulfuric acid and water on a water bath until the product dissolves. Pour into water and warm. *o*-Nitroaniline separates upon cooling in the form of orange needles.

Detection of iodide. A test for iodides proposed by Feigl and Frankel[1] depends upon the fact that *o*-nitroaniline, its isomers, or other primary aromatic amine forms a diphenyl derivative with bromobenzene in the presence of cuprous iodide or a mixture of copper and potassium iodide. This reaction is shown by the equation

$$O_2N—C_6H_4—NH_2 + C_6H_5Br \rightarrow O_2N—C_6H_4—NH—C_6H_5 + HBr$$

It nas been shown that the presence of iodide alone is sufficient to accelerate the rate of this reaction, which may be used indirectly to detect iodides. The test depends upon the formation of bromine from the hydrogen bromide formed in the reaction.

Procedure. To each of two 50-ml. flasks, add 1.5 g. of *o*-nitroaniline, 0.5 g. potassium carbonate and 6 g. of bromobenzene. Then add a drop of the solution to be tested to a boiling stone and evaporate to dryness. Add this stone to one of the flasks, and then boil the contents of both flasks gently for 20 minutes with reflux condensation. Cool and extract with absolute ether. The residue contains potassium carbonate, and some potassium bromide if iodide was present. Dissolve the residue in 10 ml. of water, add to the ether extract in a separatory funnel, and shake thoroughly until the aqueous layer is colorless. Place 8 ml. of the colorless aqueous solution in a test tube. Add 3 ml. of 2 N hydrochloric acid, 2 ml. of chloroform and 5 ml. of chlorine water. Shake well and compare the chloroform layers of the two solutions. If iodide was present in the original solution to be tested, a more intense bromine color will appear in the solution containing the unknown, since more bromobenzene reacts with *o*-nitroaniline in the presence of iodides. This results in the formation of a greater quantity of potassium bromide than in the absence of the catalyst.

By means of this reaction 0.05γ of iodide may be detected in 1 drop of a solution containing 1 mg. of iodide per liter.

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[1] F. Feigl and E. Frankel, *Z. anal. Chem.* 91, 12-14 (1932); *C.A.* 27, 683 (1933).

p-NITROANILINE

$C_6H_6O_2N_2$ Mol. Wt. 138.12 Beil. Ref. XII, 711.

$$O_2N—C_6H_4—NH_2$$

Use: Detection of ammonia.

p-Nitroaniline occurs as a bright yellow powder. It melts at 146-148° C. It is only very slightly soluble in cold water, but is much more soluble in hot water. It is slightly soluble in alcohol and ether, but is readily soluble in benzene and methyl alcohol.

Preparation: Mix 25 g. of acetanilide, 25 ml. of acetic acid and 50 ml. of sulfuric acid and cool in a freezing mixture. Add gradually from a separatory funnel 10 ml. of fuming sulfuric acid at such rate that the temperature does not exceed 20° C. Stir the mixture for an hour with the aid of a mechanical stirrer, and pour the reaction mixture onto ice. Dilute the material with water, allow to stand for some time and filter. Wash and dry on a porous plate. Heat the *p*-nitroacetanilide with twice its weight of a solution prepared by mixing equal volumes of sulfuric acid in water until the liquid remains clear on diluting with water. Dilute with water and precipitate *p*-nitroaniline by the addition of an excess of sodium hydroxide or ammonia. Allow to cool, filter, wash, and recrystallize from boiling water.[1]

Detection of ammonia. This reagent is used for the detection of ammonia by first converting to the diazo compound with the aid of nitrous acid. For the details of this procedure, see section on *p*-nitrodiazobenzene.

1. Bender and Erdmann, *Chemische Präparatenkunde,* Vol. II, p. 438.

o-PHENETIDINE

Synonym: 2-Aminophenetole

$C_8H_{11}ON$ Mol. Wt. 137.18 Beil. Ref. XIII, 359.

$$C_2H_5O—C_6H_4—NH_2$$

Use: Determination of aluminum.

Separation of aluminum from iron.

o-Phenetidine is a colorless, oily liquid, which rapidly becomes brown on exposure to light and air. It boils at 228-230° C. It is insoluble in water, but dissolves in alcohol.

Preparation: Mix 100 g. of 2-nitrophenetole with 200 g. of zinc to form a paste, and add this gradually in small quantities to a mixture containing 300 g. of concentrated sulfuric acid and 700 ml. of water. The reaction is accelerated by adding a few drops of copper sulfate solution and frequent shaking.

Determination of aluminum. An alcoholic solution of *o*-phenetidine yields no precipitate with manganese, zinc, magnesium and ferrous ions, but with cobalt and nickel a partial precipitation occurs. With ferric ions a gradual precipitation of ferric hydroxide takes place in dilute solutions, but in more concentrated solutons *o*-phenetidine is oxidized to a violet compound; eventually a black condensation product precipitates.

A brown or yellowish precipitate of somewhat variable composition is obtained when *o*-phenetidine is added to solutions of aluminum salts.[1] Using this reaction, aluminum may be determined in the presence of iron by means of the following procedure.

Procedure. Place the slightly acid solution to be analyzed in an Erlenmeyer flask and saturate with hydrogen sulfide for about 10 minutes. Expel the excess hydrogen sulfide with a stream of carbon dioxide. Add ammonium carbonate until a slight, permanent precipitate of aluminum hydroxide is formed, and then carefully add dilute hydrochloric acid until the precipitate is just dissolved. To this solution, add a 5 per cent alcoholic solution of *o*-phenetidine until at least 10 times as much *o*-phenetidine as aluminum is present. Stopper the flask and heat to 80° C. Allow to stand for a short time and filter through a filter containing a little filter paper pulp. Ignite and weigh as aluminum oxide.

1. K. Chalupny and K. Breisch, *Z. angew. Chem.* 35, 233-4 (1922); *C.A.* 16, 2460 (1922).

p-PHENETIDINE Synonym: *p*-Aminophenetole, *p*-aminoethoxybenzene

$C_8H_{11}ON$ Mol. Wt. 137.18 Beil. Ref. XIII, 436.

$$C_2H_5O—C_6H_4—NH_2$$

Use: Detection of copper, ferricyanide, ferrocyanide, iron, manganese, vanadium and zinc.

Determination of chromate and vanadium.

p-Phenetidine is a colorless liquid, which becomes red or brown upon exposure to air and light. It has a sp. gr. of 1.0652 and boils at 253-255° C. It is insoluble in water but is soluble in alcohol.

Preparation: *p-nitroethoxybenzene:* Place 3.3 g. of sodium, cut into small pieces, and 125 ml. of absolute alcohol in a 500 ml. flask, which is fitted with a reflux condenser. Allow the mixture to stand until the sodium is dissolved. Then add 20 g. of *p*-nitrophenol and 16 g. of ethyl bromide and heat on a water bath for 12 hours. After about 6 hours, add an additional 5 g. of ethyl bromide. After the 12-hour heating period, remove the excess alcohol and ethyl bromide by distilling from a water bath, and add to the residue an excess of dilute sodium hydroxide solution. Extract 2 or 3 times with ether, and shake the ether solution with a little sodium hydroxide solution. Separate the mixture, and dry the ether extract over calcium chloride. Remove the ether by distillation and crystallize the product from a mixture of equal parts of water and alcohol.

p-Phenetidine: Place 13 g. of *p*-nitroethoxybenzene, 16 g. of tin, and 80 ml. of concentrated hydrochloric acid in a 500 ml. flask and heat the mixture on a water-bath until the reaction begins. Remove the flask from the water-bath if the reaction becomes too violent. When the first reaction has subsided, replace the flask on the water-bath and heat until all the tin is dissolved. When solution is complete, cool, and separate the crystalline mass by filtration. A further quantity of crystals may be obtained by evaporating the filtrate. Add a solution containing 30-35 g. of sodium hydroxide to the moist crystalline product until most of the stannic oxide has dissolved. Then extract the alkaline solution 2 or 3 times with ether until a small portion of the ether extract leaves no residue on evaporation. Dry the ether solution with potassium carbonate, and remove the ether by distillation. Distill the dark-colored oil *in vacuo*. The boiling point is 160-165° C. at 12 mm.[1]

Detection of vanadium. Small quantities of vanadium may be detected by its catalytic effect upon reactions between *p*-phenetidine and certain oxidizing agents, such as potassium chlorate, potassium bromate and potassium periodate.

p-Phenetidine reacts with potassium chlorate or potassium bromate in dilute hydrochloric acid solutions very slowly, if at all, but the reaction is catalyzed by the presence of less than 1γ of vanadium. Szebelledy and Ajtai [2-6] have used this reaction as the basis for a sensitive test for vanadium.

Procedure. Add 1 ml. of 0.1 per cent *p*-phenetidine hydrochloride and 1 ml. of a saturated solution of potassium chlorate to a little of the solution to be tested and dilute the mixture to 5 ml. Prepare a blank using the same reagents with distilled water instead of the solution to be tested. Place both mixtures in a water-bath and heat for a short time. The solution containing vanadium becomes violet in color, whereas the blank remains colorless or pale violet. As little as 1γ of vanadium can be detected in this way.

Potassium bromate or periodate may be substituted for potassium chlorate. If potassium periodate is used as the oxidizing agent, proceed as follows:

Procedure. Add 0.5 ml. of a 0.1 per cent solution of *p*-phenetidine hydrochloride, and 0.2 ml. of a saturated solution of potassium periodate to a little of the solution to be tested and dilute to 5 ml. Prepare a blank and proceed as above. Vanadium is indicated by the appearance of a violet color.

Ferrous and stannous ions interfere and must be removed. When potassium bromate is used as the oxidizing agent, mercury, copper, chromium, manganese, bromide and iodide interfere. Interference due to the presence of ferric ions is eliminated by the addition of 0.05 g. of sodium hydrogen fluoride, and interference due to lead is prevented by adding 0.05 g. of sodium sulfate. If chromic salts are present, add 0.05 g. of sodium acetate, then 10 ml. of a saturated potassium periodate solution and 0.2 ml. of 0.1 per cent *p*-phenetidine hydrochloride solution.

The catalytic activity of vanadium in the reaction between *p*-phenetidine and potassium chlorate or bromate is enhanced by the addition of potassium acid tartrate to the reaction mixture.[2,17] The test is modified as follows:

Procedure. Add 0.05 g. of solid potassium acid tartrate, 1 ml. of a 1 per cent solution of *p*-phenetidine in dilute hydrochloric acid, and 1 ml. of saturated potassium chlorate solution or 0.5 ml. of saturated potassium bromate solution to a little of the solution to be tested, and then add sufficient water to make the total volume 5 ml. Prepare a blank and warm both mixtures in a water-bath. A violet color indicates vanadium. Lead ions interfere but this interference is prevented by addition of 0.1 g. of sodium sulfate. Ferric ions do not interfere if 5 g. of sodium hydrogen fluoride is added. Iodides and ammonium chlorostannate interfere.

The catalytic effect of vanadium on the reaction between *p*-phenetidine and potassium chlorate, potassium bromate and potassium periodate is also activated by the presence of 8-hydroxyquinoline.[3] With potassium bromate or periodate as little as 0.01γ of vanadium may be detected in the presence of 8-hydroxyquinoline, while the effect is even greater when potassium chlorate is used. Tests may be obtained with as little as 0.001γ of vanadium by the reaction between *p*-phenetidine and potassium chlorate in the presence of 8-hydroxyquinoline. Lead, silver, copper, and ammonium chlorostannate, however, interfere.

Pyrocatechol also is used to increase the catalytic effect of *p*-phenetidine in the vanadium reaction. In this way 0.001γ of vanadium may be detected. Szebelledy and Ajtai[5] have based a method for the determination of small quantities of vanadium upon the catalytic effect of the latter in a reaction between *p*-phenetidine and potassium bromate.

Procedure. Place 1 ml. of the solution to be tested in a carefully cleaned test tube, and mix with 1 ml. of 0.1 per cent *p*-phenetidine, 1 ml. of freshly prepared pyrocatechol solution and sufficient water to make the total volume 4 ml. Shake the mixture and quickly blow in 1 ml. of 5 per cent potassium bromate solution from a micropipet. Start a stop watch immediately. Transfer 1 ml. of the reaction mixture to the optical vessel of a photometer, and note the time required for the galvanometer needle to reach the scale division marked 50. By referring to charts prepared with solutions containing known quantities of vanadium, the amount of vanadium in the unknown can be calculated.

An alternate procedure consists in measuring the times taken for the needle to show divisions 90, 80, 70, etc. This method may be used to determine as little as 0.0006γ of vanadium.

Detection of manganese. Szebelledy and Bartfay[7,8,15] have detected manganese by a procedure similar to that employed for the detection of vanadium. Manganese catalyzes the reaction between solutions of *p*-phenetidine and potassium iodate to form a violet-colored compound.

Procedure. Place 4.5 ml. of the solution to be tested in a test tube, and in a similar tube place an equal volume of distilled water. To each add 0.5 ml. of a freshly prepared 20 per cent solution of potassium iodate and 0.1 ml. of a 0.1 per cent solution of *p*-phenetidine hydrochloride and shake. A violet color appears in the solution containing manganese. The blank test remains colorless for about 10 minutes, while a color appears in the presence of manganese within 2-3 minutes. A coloration is obtained with as little as 0.001γ of manganese.

Detection of iron. Iron is detected by the following reaction employing *p*-phenetidine and 2,2'-dipyridyl.[9,10]

Procedure. Place a few drops of the solution to be tested in a 5 ml. porcelain microcrucible, and add 0.1 ml. of 0.01 per cent solution of *p*-phenetidine hydrochloride, 1 drop of a 2 per cent alcoholic solution of 2,2'-dipyridyl, and 0.1 ml. of a 0.2 per cent solution of hydrogen peroxide measured exactly by means of a micropipet. A red color appears immediately in the presence of as little as 0.001γ of ferrous ion, but the color appears only after 1-5 minutes on a water-bath if ferric iron is present.

Detection of copper. *p*-Phenetidine is used for the detection of small quantities of copper.[11]

Procedure. Place 0.1 ml. of the solution to be tested in a small crucible and place 0.1 ml. of distilled water in a second crucible. To each add 0.1 ml. of 0.01 per cent *p*-phenetidine hydrochloride, 0.1 ml. of 0.2 per cent hydrogen peroxide, and dilute each mixture to 0.5 ml. Then heat on a water-bath and observe any color change. A violet color appears in the solution containing copper within 1-5 minutes, while the blank test remains colorless during the first 5 minutes. The test is sensitive to 0.01γ of copper.

Sodium, potassium, ammonuim, magnesium, calcium, strontium, barium, cobalt, nickel, manganese, zinc, aluminum, chromium, arsenic, antimony, tin, silver, lead, mercury, bismuth, cadmium and sulfates do not interfere. The disturbing effect of chloride, bromide and iodide is eliminated by the addition of a solution of silver nitrate.

Detection of zinc. Small quantities of zinc are detected by means of a test proposed by Szebelledy and Tanay.[12] The test is carried out as follows:

Procedure. Mix on a spot plate 6 drops of a freshly prepared 2 per cent solution of potassium ferricyanide with 2 drops of N sulfuric acid and 12 drops of 1 per cent *p*-phenetidine hydrochloride solution. Transfer 0.1 ml. of the resulting brownish-yellow mixture to another depression in the white spot plate and carefully add about 0.01 ml. of the solution to be tested. A blue precipitate or coloration appears at the zone of contact if zinc is present. In this way 0.05γ of zinc can be detected.

This test depends upon the formation of a precipitate of $K_2Zn_2(Fe(CN)_6)_2$ from the potassium ferrocyanide which is present in the ferricyanide reagent. The removal of the ferrocyanide by the zinc ion increases the oxidizing power of the ferricyanide, which then oxidizes *p*-phenetidine to the colored oxidation product, which in turn is adsorbed by the precipitate.

Ammonium, potassium, sodium, magnesium, calcium, strontium and barium ions do not interfere, and the test may be carried out in the presence of mercury, arsenic, antimony, aluminum, cadmium, manganese, and chromium by comparing the results with blank tests upon solutions containing these ions. Silver, lead, bismuth and tin interfere, but may be removed by precipitation. The test fails completely, however, in the presence of iron, cobalt, nickel and copper.

Detection of cerium. If a drop of a solution of a ceric salt is added to a drop of a saturated aqueous solution of *p*-phenetidine, a violet color is formed. This reaction serves to detect 1γ of cerium. Iron, chromium, antimony, copper and vanadium in higher states of oxidation give similar tests.[16]

Detection of ferrocyanide and ferricyanide. Ferrocyanide and ferricyanide may be detected by a reaction which is based upon the fact that the very slow oxidation of *p*-phenetidine by hydrogen peroxide is catalyzed by the presence of ferricyanides and ferrocyanides.[13]

Procedure. Place 4 ml. of solution to be tested in a clean test tube and to a second test tube of the same size add 4 ml. of distilled water. To each tube add 0.5 ml. of a 0.025 per cent solution of *p*-phenetidine in hydrochloric acid and

0.5 ml. of 0.2 per cent hydrogen peroxide solution. Heat both tubes on a water-bath. An intense red-violet coloration appears within 1-10 minutes if ferricyanide or ferrocyanide is present, but the blank test shows very little color after 10 minutes.

Determination of chromates. Vavilov[14] has suggested the use of *p*-phenetidine hydrochloride for the colorimetric determination of soluble chromates.

Reagent. Prepare a 1 per cent solution of *p*-phenetidine hydrochloride in 0.045 N hydrochloric acid.

Procedure. Add 0.3 ml. of the reagent to 0.1-0.2 ml. of the material to be tested and then dilute the mixture to 100 ml. Compare the resulting color with a standard prepared by treating a solution of potassium dichromate of known concenration in the same manner. The test fails in the presence of silicates, orthophosphates, reducing agents and oxidizing agents.

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o-PHENYLENEDIAMINE

Synonym: *o*-Diaminobenzene

$C_6H_8N_2$ Mol. Wt. 108.14 Beil. Ref. XIII, 6.

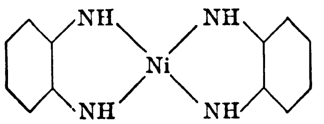
$$C_6H_4(NH_2)_2$$

Use: Detection of nickel and vanadium and differentiation of ozone from nitrous acid and hydrogen peroxide.

o-Phenylenediamine is a brownish-yellow crystalline solid. It melts at 99-101° C. and boils at 256-258° C. It is slightly soluble in water, but is freely soluble in alcohol, ether and chloroform.

Preparation: Mix 69 g. of *o*-nitroaniline, 40 ml. of 20 per cent sodium hydroxide and 200 ml. of 95 per cent ethyl alcohol in a three-necked liter flask. Fit with a mechanical stirrer and a reflux condenser, and stir vigorously while heating on a water-bath until the mixture boils. Remove the source of heat and add 130 g. of zinc dust in 10-g. portions at such intervals that the mixture continues to boil. When all zinc has been added, reflux with stirring for 1 hour. Filter the hot mixture with suction and extract the zinc residue with two 150-ml. portions of hot alcohol. Combine the filtrates and add 2-3 g. of sodium hydrosulfite and evaporate under reduced pressure on a steam bath to a volume of 125-150 ml. Cool thoroughly in an ice-salt bath and filter the pale yellow crystals. Wash with a small amount of ice water and dry in a vacuum desiccator. Dissolve in 150-175 ml. of hot water containing 1-2 g. sodium hydrosulfite and treat with decolorizing charcoal. Cool in an ice-salt mixture, filter with suction, and wash with 10-15 ml. of ice water.[1,2]

Detection of nickel. An amorphous bluish-purple precipitate, having the composition $Ni[C_6H_4(NH)_2]_2$, is formed when *o*-phenylenediamine is added to an ammoniacal solution of a nickel salt.[3-5] The properties of this compound indicate that the nickel is in the tetravalent state. The following probable formula has been suggested, although there are several objections to this formulation.



Hieber and coworkers,[8] however, state that the complex may exist in concentrated solutions, but in dilute solutions is completely dissociated into its constituents. Further, the diamine occupies only one coordination position.

This compound is very stable, is insoluble in the organic solvents, but is partially soluble in pyridine, quinoline, piperidine and aniline with which it yields purple colors. The compound is not decomposed with bases, but reacts with alkali sulfides to yield black nickel sulfide. It dissolves in mineral acids and acetic acid to yield red-brown solutions, and reacts with potassium iodide with the immediate liberation of iodine. Stannous chloride is partially oxidized by this substance.

Differentiation of ozone from nitrous acid and hydrogen peroxide. Erlwein and Weyl[6] have used *o*-phenylenediamine to differentiate ozone from nitrous acid and hydrogen peroxide. The colorless reagent in dilute hydrochloric acid is colored a marked Burgundy-red by a few bubbles of ozone. The same color is obtained if the reagent is dissolved in an alkaline solution. Nitrites and hydrogen peroxide do not react with *o*-phenylenediamine in an alkaline solution.

Reagent. The reagent is prepared by dissolving 0.1-0.2 g. of *o*-phenylenediamine hydrochloride in 90 ml. of water and 10 ml. of 5 per cent sodium hydroxide solution. This reagent must be freshly prepared, since in the presence of oxygen the solution soon becomes colored.

Procedure. The gas suspected of containing ozone is passed slowly through 25 ml. of the above reagent. As little as 0.08 mg. of ozone will yield a yellowish-brown color within 5 seconds. With higher concentration of ozone a Burgundy-red color is observed.

Detection of vanadium. *o*-Phenylenediamine hydrochloride reacts with a dilute solution of ammonium vanadate to give an orange color. This reaction is sensitive to one part of ammonium vanadate to 10,000 parts of solution.[7]

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m-PHENYLENEDIAMINE

Synonym: *m*-Diaminobenzene

$C_6H_8N_2$ Mol. Wt. 108.14 Beil. Ref. XIII, 33

$C_6H_4(NH_2)_2$

Use: Detection of bromate, bromide, chromate, copper, dichromate, gold, hypobromite, iron, oxygen, ozone and platinum.

Determination of active chlorine, chromium, iridium, nitrite and palladium.

m-Phenylenediamine consists of white crystals which become red on exposure to air. It melts at 62-63° C. and boils at 284-287° C. It is soluble in water, alcohol and ether. The compound should be stored in a tightly stoppered bottle and protected from light.

Preparation: Dissolve 30 g. of stannous chloride ($SnCl_2 \cdot 2H_2O$) in 50 ml. of concentrated hydrochloric acid, and to this gradually add 5 g. of *m*-nitroaniline. Heat on a water-bath for about 30 minutes, or until no precipitate forms when water is added. Dilute with 500 ml. of water and heat to boiling, and pass in a stream of hydrogen sulfide until all the tin is precipitated. This requires about 30-45 minutes. Allow the mixture to stand overnight and decant off the clear supernatant liquid, and then filter the residue with suction, using a double filter. Concentrate the clear filtrate on a water-bath until crystals begin to form, and allow the solution to cool. Filter off the crystals of the *m*-phenylenediamine hydrochloride.[1,2]

m-Phenylenediamine may also be prepared by the reduction of *m*-dinitrobenzene.

Preparation: Place 150 ml. of water in a vessel equipped with a stirrer, and heat to 95° C. Add 100 g. of *m*-dinitrobenzene, and then add gradually with stirring 10 ml. of concentrated hydrochloric acid and 120 g. of fine iron powder. Continue the reaction until the liquid loses its yellow color as shown by spotting filter paper. Add a solution of sodium carbonate until the mixture is alkaline, and heat to boiling. Filter, boil the iron residue with water, and again filter. Combine the filtrates, and concentrate by evaporation. Add concentrated hydrochloric acid to precipitate the amine hydrochloride. Cool the mixture, filter, and dry the product.

Detection of nitrites. *m*-Phenylenediamine reacts with nitrous acid to form a brownish-yellow dye known as Bismark brown. This is a mixture consisting essentially of the products resulting from the coupling of diazotized and tetrazotized *m*-phenylenediamine with unreacted *m*-phenylenediamine. The coupling takes place very rapidly according to the following reactions.

$$H_2N—C_6H_4—N\equiv N—X + C_6H_4(NH_2)_2 \rightarrow H_2N—C_6H_4—N{=}N—C_6H_3(NH_2)_2$$

and

$$X—N{=}N—C_6H_4—N{=}N—X + 2C_6H_4(NH_2)_2 \rightarrow (H_2N)_2C_6H_3—N{=}N—C_6H_4—N{=}N—C_6H_8(NH_2)_2$$

The formation of these dyes has been used by Griess and many others for the detection and colorimetric estimation of nitrite.[3-15,36]

The following procedure is used for the detection of nitrous acid or nitrites.[16]

Reagent. Place 2 g. of *m*-phenylenediamine hydrochloride in a flask or bottle which is fitted with a ground glass stopper, and add 100 ml. of 20 per cent ammonia and 5 g. of animal charcoal. When ready to use, decant a little of this mixture through a filter and use the clear filtrate.

Procedure. Add 5 drops of the reagent to 5 ml. of 10 per cent sulfuric acid and mix with 5 ml. of the solution suspected of containing nitrite. Shake well and warm slightly. A brown color appears if nitrites are present.

Determination of nitrite. Prescher[17] and others[13,18,19] have used the reaction of *m*-phenylenediamine with nitrous acid, in which Bismark brown is formed, for the detection and colorimetric determination of nitrite in meats. The following procedure is used for this purpose:[17]

Reagent. Dissolve 0.5 g. of *m*-phenylenediamine in 30 ml. of water containing 3 ml. of dilute sulfuric acid, and dilute to 100 ml.

Procedure. Shake 30 g. of finely crushed meat with 100 ml. of moderately warm water which is acidified with 1 ml. of dilute sulfuric acid (1:3). Filter and add 1 drop of the reagent to 1 ml. of the resulting clear filtrate. If nitrites are present the yellow to brown color of Bismark brown appears.

The intensity of the color formed when solutions of nitrites react with *m*-phenylenediamine depends upon the quantity of nitrites present; hence, this reaction is used for the colorimetric determination of nitrite. Various investigators have used this method for the determination of nitrites in foods, particularly in meats, but according to Auerbach and Riess[18] the results obtained by many of the earlier procedures are inaccurate, due chiefly to the influence of chloride upon the color reaction. These authors claim to have eliminated this difficulty by the addition of acetic acid and sodium acetate, and propose the following method.

Procedure. The filtered meat extract is first treated with colloidal ferric hydroxide to precipitate proteins and coloring matter, which are removed when the mixture is filtered. Treat 50 ml. of the filtrate obtained by extracting 1.8-2.0 g. of meat with 1 ml. of 10 per cent sodium acetate, 0.2 ml. of 30 per cent acetic acid, and 1 ml. of 1.5 per cent *m*-phenylenediamine hydrochloride solution containing a few drops of acetic acid. Compare the resulting color with that obtained with standard solutions of pure sodium nitrite containing 0.01 to 0.3 mg. of nitrite in 50 ml., and to which 0.25 g. of sodium chloride has been added, before treating as described above.

According to Blanc[20,21] the determination of nitrite by methods employing *m*-phenylenediamine are more satisfactory than the procedure of Trommsdorff,[22] which depends upon the liberation of iodine from zinc iodide by the action of nitrous acid. In the latter method, oxygen of the atmosphere acts upon zinc iodide to liberate free iodine, thereby introducing some error.

Pieters and Mannens[23] have used *m*-phenylenediamine for the determination of nitrous acid in concentrated sulfuric acid. Milligan[24] has conducted an exhaustive study of the reduction products of nitric acid, and has used *m*-phenylenediamine for the determination of nitrous acid in his analyses.

Reactions with metals. Katakouzinos[25] has studied the reactions of aqueous solutions of various ions with *m*-phenylenediamine and has reported the following results:

(a) Dilute solutions of iron salts yield a rose-color with the reagent, and this color is deeper in more concentrated solutions.

(b) Solutions of copper salts give a rose-red color, which changes to green on the addition of ammonia.[88]

(c) Dilute solutions of chromates and dichromates react with the reagent to give a deep brown to brownish-red color. In more concentrated solutions a dark brownish precipitate is obtained. If to a neutral or acid solution containing a chromate or dichromate, the reagent and ammonia are added and the solution boiled, a yellow color is obtained. *m*-Phenylenediamine gives a reaction with chromates and dichromates in dilutions greater than 1:2,000,000.

To detect chromium in the presence of iron salts, the mixture is treated with sodium peroxide and filtered, and the test is then applied by adding the reagent to the clear filtrate.[25] *m*-Phenylenediamine does not react with salts of aluminum, manganese, zinc, cadmium, nickel and cobalt.

Reactions with platinum and the platinum metals. Large well-formed crystals are obtained when a weakly ammoniacal solution of platinic chloride containing *m*-phenylenediamine is allowed to evaporate in the dark.[26] The test is obtained by adding a fragment of the reagent to a drop of the solution to be tested. On standing for a short time, long, slender, bright yellow needle-shaped crystals develop around the edge of the drop.

Whitemore and Schneider[27] have studied the reaction of a 10 per cent solution of *m*-phenylenediamine with solutions of salts of the platinum metals, and have reported their results in Table 48.

TABLE 48.—REACTIONS OF *m*-PHENYLENEDIAMINE WITH THE PLATINUM METALS

Test Material 2 Per Cent Solution

Reagent: *m*-Phenylenediamine—10 Per Cent Solution

Test Material	Description
$RuCl_4$	No apparent reaction.
$RhCl_3$	An amorphous, reddish-brown, precipitate forms.
$PdCl_2$	A very dense, yellowish-brown, amorphous precipitate forms.
Na_2OsCl_6	No apparent reaction.
$IrCl_4$	A reddish-brown, flocculent precipitate forms.
H_2PtCl_6	On standing, radiates of extremely long crystals develop at the edge of the drop. Similar forms also develop throughout thedrop, though these are not made up of such large crystals.
$AuCl_3$	A dark, amorphous precipitate forms.

Detection and determination of gold. When a 0.5 per cent solution of *m*-phenylenediamine in sulfuric acid is added to a dilute solution of gold chloride (approximately 0.5 per cent) there is formed, depending upon the concentration of the gold solution, a yellow to dark brown color. This color is caused by the reduction of the gold salt to colloidal metallic gold. A 0.005 per cent solution of gold chloride gives a violet color. By means of this reaction gold may be detected.[28,29,37] This reaction may also be used for the colorimetric determination of gold.

Procedure. To the solution of gold in a cyanide solution, add concentrated hydrochloric acid to destroy the cyanide and convert the gold to gold chloride. Add 5 ml. of a 0.5 per cent solution of *m*-phenylenediamine and mix well. Next add 6 N sulfuric acid in small portions, with mixing after each addition, until the color attains a maximum. Compare with standards similarly prepared.

Detection of bromide, hypobromite and bromate. Bromine is readily detected in concentrations as low as 0.5γ per ml. by means of the characteristic crystalline precipitate which it yields with a solution of *m*-phenylenediamine in 5 per cent sulfuric acid. The test is carried out by liberating bromine from bromides, hypobromites and bromates in any suitable manner, and exposing a drop of the reagent in a watch glass to the action of the resulting vapors. Chloride and iodide do not interfere as long as no large quantity of solid iodine is allowed to deposit in the drop of solution to be tested. Bromates are best reduced by means of hydrazine sulfate.[30]

Determination of active chlorine. Solutions of chlorine and hypochlorites containing more than 0.2 p.p.m. of chlorine react with *m*-phenylenediamine to give a distinct pink coloration. This color may be used for the determination of active chlorine in water. According to Harral and Jaffe,[31] *m*-phenylenediamine is more reliable than *o*-tolidine and benzidine if nitrite is likely to be present. Both benzidine and *o*-tolidine give yellow colors with nitrites. This appears to be due to the partial hydrolysis of the diazonium salt in dilute solutions to form a hydroxy compound which couples with the diazonium salt.

Detection of ozone. A colorless solution of *m*-phenylenediamine hydrochloride turns to a marked Burgundy red when treated with a few bubbles of ozone. The same color appears when an alkaline solution of the reagent is used. Nitrite and hydrogen peroxide, however, do not react with the *m*-phenylenediamine in an alkaline solution. By means of the following procedure ozone may be detected and differentiated from nitrous acid and hydrogen peroxide.[32,34]

Procedure. Allow the gas suspected of containing ozone to pass through 25 ml. of a solution containing 0.1-0.2 g. of *m*-phenylenediamine hydrochloride in 90 ml. of water and 10 ml. of 5 per cent sodium hydroxide. This solution must be freshly prepared since oxygen causes the appearance of a distinct color. A yellowish-brown color is formed within 5 seconds with as little as 0.08 mg. of ozone. With a greater concentration of ozone the color is finally Burgundy red.

Detection of oxygen. A solution containing 1 g. of *m*-phenylenediamine in 100 g. of alcohol is colored yellowish-brown by the introduction of oxygen. Cazeneuve [35,39] used this reaction for the detection of oxygen, but the method seems to be of little value since various oxidizing agents give similar color reactions with the reagent.

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p-PHENYLENEDIAMINE

Synonym: *p*-Diaminobenzene, Ursol D

$C_6H_8N_2$ Mol. Wt. 108.14 Beil Ref. XIII, 61

$$C_6H_4(NH_2)_2$$

Use: Detection of ammonia, copper, gold, hydrogen sulfide, iron, magnesium, oxidizing agents, ozone, sulfur dioxide and vanadium.

Determination of chromium.

p-Phenylenediamine consists of white, slightly red crystals which darken on exposure to air. It melts at 147° C., and boils at 267° C. It is soluble in 100 parts of cold water, and is soluble in alcohol, chloroform and ether.

Preparation: Mix 100 ml. of water and 100 g. of powdered iron and add 5 ml. of concentrated hydrochloric acid. Heat to 95° C., and add gradually and with stirring 100 g. of *p*-nitroaniline. Cool if necessary to keep the temperature at 95° C. Continue the reduction until the solution loses its yellow color. This point is determined by spotting a piece of filter paper with the liquid. Add a solution of sodium carbonate until the mixture is alkaline. Filter, and evaporate the filtrate until the base crystallizes.[18]

p-Phenylenediamine may also be prepared by the reduction of *p*-nitrosoaniline with tin and hydrochloric acid.[1]

Detection of vanadium. Dark colored complexes which contain 7.80-37.72 per cent V_2O_3 are formed when concentrated solutions of *p*-phenylenediamine are added to cold solutions of vanadium salts. The colors of these complexes range from yellow to dark green. The color in neutral solution is yellow, but in hydrochloric acid solutions a pink to red color is obtained. By means of these reactions as little as 0.005 mg. of vanadium in 10 ml. of water can be detected.[2,8]

Szebelledy and Ajtai[4] have determined vanadium by microchemical methods by means of its catalytic effect upon certain oxidation reactions. A very sensitive test based upon this principle depends upon the oxidation of a mixture of *α*-naphthol and *p*-phenylenediamine by means of potassium chlorate.

Procedure. To the solution to be tested, add 1 ml. of a 0.1 per cent solution of *α*-naphthol, 1 ml. of a 0.1 per cent solution of *p*-phenylenediamine and 1 ml. of a saturated solution of potassium chlorate, and then dilute with water to 5 ml. Prepare a blank test by mixing the reagents only and diluting with water to 5 ml. Place the tubes containing both mixtures on a water-bath for a few minutes. The solution containing vanadium assumes a brownish-red color, while the blank solution remains colorless or slightly pink. This reaction is given with as little as 0.1γ of vanadium.

The disturbing effect of tin as ammonium chlorostannate is eliminated by adding 0.1 g. of potassium oxalate. Silver also interferes, but is removed by precipitation with sodium chloride. The above procedure cannot be used in the presence of lead.

Detection of copper and iron. Copper is detected by means of the black precipitate of copper thiocyanate-phenylenediamine which is formed when potassium thiocyanate and *p*-phenylenediamine are added to an ammoniacal or neutral solution of a copper salt.[5,15] The copper compound contains 25.08 per cent of copper, and appears to be a coordination complex in which the *p*-phenylenediamine is linked to the copper atom. The black precipitate dissolves in acids to give a black solution. The following procedure is used to detect copper in a systematic scheme of analysis:

Procedure. To a few drops of the ammoniacal solution of copper obtained after the removal of bismuth in the conventional scheme of analysis, add 5 ml. of a saturated solution of potassium thiocyanate and 2-3 drops of an aqueous solution of *p*-phenylenediamine. A black precipitate forms with as little as 1 part of copper in 100,000 parts of solution.

Cadmium, which is normally present with copper at this stage of the analysis, does not interfere. No precipitate is given by cobalt, manganese, iron, magnesium, aluminum, chromium or nickel. Cadmium and zinc form white precipitates, but these are soluble in acid and ammoniacal solutions. Mercury gives a gray precipitate which is soluble in ammonia but is insoluble in acid solutions. Silver gives a white precipitate which is soluble in acid but insoluble in ammonia. With the exception of silver, therefore, all common metals may be separated from copper by this procedure.

Quartaroli[6] has used *p*-phenylenediamine as a sensitive reagent for the detection of copper and iron in biological research. *p*-Phenylenediamine reacts with solutions of copper salts to yield a brown color which gradually changes to violet, and which suddenly changes into a deep violet color on addition of 2 drops of concentrated hydrochloric acid. Ferric iron gives a brown color with *p*-phenylenediamine, but it does not change to violet on the addition of hydrochloric acid. Manganese gives a negative reaction.

Detection of gold. Many substances reduce gold salts to colored colloidal solutions of gold. This reaction has been rather widely used as a means of detecting small quantities of gold. *p*-Phenylenediamine is a particularly delicate reagent for this test.[7]

Procedure. Add 1 ml. of a 0.1 per cent *p*-phenylenediamine hydrochloride solution to 10 ml. of a very dilute solution of gold chloride. A distinct yellowish-green coloration is produced with as little as 0.0005 per cent gold chloride, and a greenish color is obtained with solutions containing 0.001 per cent gold chloride.

Detection of magnesium. A reddish-violet precipitate is obtained when a few drops of a 0.5 per cent aqueous solution of *p*-phenylenediamine is added to a solution containing magnesium ions, and the mixture made alkaline by the dropwise addition of a concentrated solution of potassium hydroxide. The precipitate dissolves in dilute acids to form colorless solutions, but the color returns on the addition of a base. This reaction is used as a fairly sensitive test for magnesium.[8] Salts of the alkali metals do not interfere. Zinc and aluminum give white precipitates, but these redissolve in an excess of potassium hydroxide. Barium and strontium also yield precipitates, but they are of a different color from that of the magnesium precipitate. Calcium alone of all the common metals may be confused with magnesium, since it, too, yields a violet precipitate in the presence of *p*-phenylenediamine and potassium hydroxide. If this precipitate, however, is redissolved in a tartaric acid soluton, and more potassium hydroxide added, only magnesium precipitates with the characteristic color. As little as 0.01 per cent magnesium can be detected by this method.

Detection of ozone. Arnold and Mentzel[9] have used *p*-phenylenediamine for the detection of ozone. In the presence of ozone, the reagent is first colored yellow, then brownish-yellow, and finally a Burgundy-red. Hydrogen peroxide gives a yellow color, and nitrous acid a yellowish-red color.

Chlopin[14] has used filter paper impregnated with Ursol D, which is *p*-phenylenediamine hydrochloride, for the detection of ozone. The test paper is colored blue by ozone, while hydrogen peroxide and nitrous acid do not give this test.

Detection of oxidizing agents. When *p*-phenylenediamine is treated with certain oxidizing agents, diiminoquinone, or certain polymerization products of a violet color are formed.[10,16] Among the substances which may be detected by this reaction are hypochlorites, nitrites, permanganates, dichromates, hydrogen peroxide, chlorine, bromine and iodine. A 0.5 per cent solution of the reagent is suitable for making the test.

Detection of ammonia. The product obtained by diazotizing *p*-phenylenediamine reacts with ammonia to form a colored compound. This reaction is used as a rather sensitive test for ammonia in air or other gases.[11] The reagent is prepared by diazotizing *p*-phenylenediamine with sodium nitrite and hydrochloric acid in the usual manner, and then impregnating filter paper with the resulting solution. By means of this reagent it is possible to detect a small fraction of a mg. of ammonia in 1 liter of air. Hydrogen sulfide disturbs this reaction and must be absent.

Detection of hydrogen sulfide. Lauth[12,17] reports that a solution of hydrogen sulfide in a weakly acid solution is colored violet by the addition of *p*-phenylenediamine hydrochloride and ferric chloride.

Detection of sulfur dioxide. Sulfur dioxide may be detected by the violet-blue color which is obtained when sulfur dioxide, *p*-phenylenediamine, and a little formaldehyde are allowed to react.[13] The test is carried out in the following manner:

Procedure. Place a solution of sulfur dioxide in a test tube, add a little reagent and swirl the tube and contents gently. Hold the tube vertically and without stirring add 2-3 drops of 40 per cent formaldehyde. A violet-blue color appears at the bottom of the tube, and this gradually deepens with a reddish color appearing in the upper part of the tube. Close the tube with a finger and carefully invert. A beautiful azure color is obtained in the presence of sulfur dioxide. The color is made more permanent in highly dilute solutions by adding a few drops of nitric acid or sodium tetraborate after the color has formed.

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α-PHENYL-β-DIETHYLAMINOETHYL-*p*-NITROBENZOATE HYDROCHLORIDE

$C_{19}H_{22}O_4N_2$ Mol. Wt. 342.37

$$O_2N—C_6H_4—CO—O—CH(C_6H_5)—CH_2—N(C_2H_5)_2\cdot HCl$$

Use: Detection of nitrate and perchlorate.

α-Phenyl-β-diethylaminoethyl-*p*-nitrobenzoate hydrochloride is a white crystalline solid melting at 210-212° C.

Preparation: *α-Diethylaminoacetophenone.* Dissolve 154 g. of α-chloroacetophenone in 500 ml. of benzene, and add this mixture to a solution of 150 g. of diethylamine in 150 ml. of benzene. Allow to stand 2 days, and filter off the separated diethylamine hydrochloride. Evaporate the benzene from the filtrate, and distill the residue under reduced pressure. Collect the fraction boiling at 148-152° C./30 mm.

α-Phenyl-β-diethylaminoethanol. Dissolve 50 g. of the amino ketone in 100 ml. of alcohol, and reduce with hydrogen in the presence of a platinum catalyst prepared by the method of Adams and Voorhees.[3] The catalyst is prepared from 2.3 g. of chloroplatinic acid. Allow the reduction to run overnight. Filter off the catalyst, and remove the alcohol by heating on a steam bath. Distill the residue under reduced pressure. A small fraction distills below 149° C./22 mm.

α-Phenyl-β-diethylaminoethyl-p-nitrobenzoate hydrochloride. Add 60 g. of *p*-nitrobenzoyl chloride and 35 g. of the amino alcohol to 250 ml. of benzene contained in a flask equipped with a reflux condenser and a mechanical stirrer. Stir 3 hours, while keeping the temperature at 50-55° C. Filter the ester hydrochloride, and wash with ether. M. P. 155-156° C.

Detection of nitrates and perchlorates. α-phenyl-β-diethylaminoethyl-*p*-nitrobenzoate hydrochloride forms difficultly soluble salts with nitric and perchloric acids. These reactions are used for the detection of nitrates and perchlorates.[2]

Reagent. Dissolve 3 g. of α-phenyl-β-diethylamino-ethyl-*p*-nitrobenzoate hydrochloride in 10 ml. of water.

Procedure. Add 0.5 ml. of the above reagent and 3 drops of dilute hydrochloric acid to 5 ml. of the solution to be tested. The formation of a precipitate indicates the presence of nitrate or perchlorate.

These reactions are not as sensitive as might be desired, owing to the slight solubility of the nitrate and perchlorate salts of the reagent. At 25° C., 0.031 g. of the nitrate and 0.0296 g. of the perchlorate dissolves in 10 ml. of water.

Iodide, oxalate, thiocyanate and dichromate interfere. In the absence of such interference, a 0.005 N solution of a nitrate and a 0.0025 N solution of a perchlorate gives the test. Nitrite may also precipitate in an acid solution, but the precipitate does not form immediately in a neutral solution. In an acid solution, bromate yields an oily product with the reagent but no precipitate is obtained in a neutral solution.

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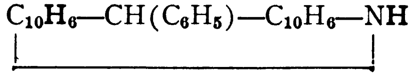
PHENYLDIHYDRODIBENZOACRIDINE

$C_{27}H_{19}N$ Mol. Wt. 357.42



$C_{10}H_6—CH(C_6H_5)—C_{10}H_6—NH$

Use: Detection of chlorates.

Detection of chlorates. Phenyldihydrodibenzoacridine has a structure which is similar in certain respects to β-dinaphthylamine except that in this compound the two β-carbon atoms are joined to a $>CH·C_6H_5$ group. For this reason it reacts with oxidizing agents in much the same manner as β-dinaphthylamine. A solution of 0.01 g. of phenyldihydrodibenzoacridine in 100 ml. of concentrated sulfuric acid possesses a reddish-yellow color with a greenish fluorescence. With this solution chlorates produce a somewhat violet-reddish-brown color, and nitrates and nitrites give no reaction immediately. After a short time a greenish-color appears with nitrites.

1. H. Sa, *Anales farm. bioquim.* **5**, 111-4 (1934); *C.A.* **30**, 6672 (1936).

PHENYLGLYCINE

Synonym: Anilinoacetic acid

$C_8H_9O_2N$ Mol. Wt. 151.16 Beil. Ref. XII, 468

$C_6H_5—NH—CH_2—CO_2H$

Use: Detection of copper.

Phenylglycine is a crystalline solid. It melts at 127-128° C. It is moderately soluble in water, and only slightly soluble in ether.

Preparation: Exactly neutralize 19 g. of chloroacetic acid in the cold with 100 ml. of 2 N sodium hydroxide solution, add 18.6 g. of aniline, and boil for a short time under reflux until the aniline is dissolved. As the mixture cools, phenylglycine separates as an oil which soon crystallizes on rubbing. Cool the mixture for some time in ice, filter with suction and wash with a little ice cold water.[1]

Detection of copper. Solutions of copper salts react with phenylglycine to give an intense green coloration. By means of this reaction it is possible to detect copper in an acetic acid medium in the presence of all metals except cerium, gold, silver and mercurous mercury. Silver and mercury are removed by precipitation with dilute hydrochloric acid, and copper is detected in the filtrate.[2]

1. J. Houben, *Ber.* **47**, 3988 (1913).
2. M. V. Gapchenko, *Zavodskaya Lab.* **9**, 1337-8 (1940); *C.A.* **35**, 2810 (1941).

PHENYLHYDRAZINE

$C_6H_8N_2$ Mol. Wt. 108.14 Beil. Ref. XV, 67

$C_6H_5—NH—NH_2$

Use: Detection of ammonia, carbon disulfide, gold, iridium, molybdenum, palladium, platinum and silver.

Determination of aluminum, chromium, molybdenum, phosphorus, selenium, thorium, titanium, tungsten and zirconium.

Phenylhydrazine is a colorless to pale yellow or red-brown liquid. It possesses a slight aromatic odor and darkens rapidly upon exposure to air. It has a sp. gr. of 1.098. It solidifies at 19° C., and boils at 241-244° C. It is sparingly soluble in water but is soluble in dilute acids and is miscible with alcohol, benzene, chloroform and ether.

Phenylhydrazine hydrochloride consists of white silky leaflets which become discolored upon exposure to air and light. This compound melts at 240-243° C. It is soluble in water and in alcohol.

Preparation. Mix 100 ml. of concentrated hydrochloric acid with 100 ml. of water and to this mixture add 47 g. of aniline. Cool well and diazotize with a solution of 38 g. of sodium nitrite in 100 ml. of water. Before diazotizing the aniline, dissolve 158 g. of neutral anhydrous sodium sulfite or 315 g. of the heptahydrate in the least possible quantity of water. Now pour the freshly prepared diazo compound rapidly into the cold sulfite solution contained in a 2-liter round bottom flask. A sample of the resulting orange-red solution should not become turbid when boiled in a test tube. In case a turbidity does develop upon boiling, add more sulfite. Next add gradually 100 ml. of concentrated hydrochloric acid in small portions with shaking. Heat on a water-bath, add a few ml. of glacial acetic acid, and then a little zinc dust. Filter while hot, and add immediately 300 ml. of concentrated hydrochloric acid to the filtrate. Allow to stand until cool. Filter with suction and press the phenylhydrazine hydrochloride as dry as possible on the funnel. Wash with 1:3 hydrochloric acid, and decompose the salt (if desired) in a separatory funnel containing 150 ml. of 4 N sodium hydroxide solution and ether. Extract the solution twice with ether, dry the ether solution with anhydrous potassium carbonate and finally distill the phenylhydrazine in vacuum. The compound boils at 120° C. at a pressure of 12 mm.[1]

Detection of molybdenum. Molybdates react with phenylhydrazine in an acid solution to give a red color or a reddish-brown precipitate. This test depends upon the fact that molybdate ions oxidize a part of the phenylhydrazine to the diazonium salt which in turn reacts with an excess of phenylhydrazine and molybdate to give a colored azo compound. This reaction was originally proposed by Spiegel and Maass[2] as a sensitive test for molybdenum.

Reagent. Dissolve 1 g. of freshly distilled phenylhydrazine in 70 ml. of 50 per cent acetic acid.

Procedure. Heat 10 ml. of the solution to be tested with 5 ml. of reagent at the boiling point for 1-2 minutes. If molybdenum is present, a red color appears. If the color is not sufficiently distinct to constitute a positive test, extract the mixture with a little chloroform, which is colored red if molybdenum is present.

This reaction is not given by tungsten, vanadium, arsenic, antimony, chromium, tin, iron, manganese and uranium.

Montignie[3] used a saturated phenylhydrazine solution acidified with sulfuric acid as a reagent for molybdates. A red color is formed with an extremely small quantity of molybdenum. A reddish-brown precipitate forms in the absence of sulfuric acid. The above reaction may also be carried out as a drop reaction.

Reagent. A 1:2 solution of phenylhydrazine in glacial acetic acid.

Procedure. Mix a drop of the solution to be tested with a drop of the reagent solution in a depression of a spot plate. A more or less deep red coloration appears, depending on the amount of molybdenum present. For small quantities of molybdenum, a blank reaction should be carried out simultaneously.

The test may also be applied by adding a drop of the reagent solution to a strip of filter paper, and, before the drop has had a chance to spread, adding a drop of the solution to be analyzed. A red ring forms about the spot within a few minutes if molybdenum is present.

By means of the spot plate procedure, 0.32γ of molybdenum at a concentration of 1:160,000 can be detected. Using spot paper, 0.13γ of molybdenum can be detected at a concentration of 1:300,000.

Rovira[4] has studied the reaction of phenylhydrazine with molybdates and reports that the test may be obtained in the presence of 55 common ions, but that lead, stannous tin, ferricyanides, and ferrocyanides interfere. The red compound formed in the reaction may be extracted with amyl alcohol or with cyclohexanol. It melts at 147° C. and has the following composition:

Mo	8.6 per cent
C	27.25 per cent
H	4.65 per cent
N	18.33 per cent
Cl	1.47 per cent
O	39.07 per cent

Montelucci and Gamboli[5] used the Spiegel and Maass[2] reaction for the detection of molybdenum in steel. This reaction is very satisfactory since it permits the identification of molybdenum in the presence of chromium.

One of the most convenient and satisfactory methods for detecting molybdate in the presence of tungstate is by means of a reaction with phenylhydrazine.[6]

Reagent. Dissolve 1 part of phenylhydrazine in 4 parts of 50 per cent acetic acid.

Procedure. Neutralize the tungstate solution which is to be tested for molybdate, heat to boiling, and add a large excess of the phenylhydrazine reagent. A bright red color is obtained at once with as little as 100 p.p.m. of molybdenum. By allowing to stand a short time, the color is obtained with only 10 parts per million. This color is intensified by extracting with ethyl acetate or chloroform.

Rice and Yerkes[7] have studied the sensitivities of various reactions which have been used for the identification of molybdenum, and report their results in Table 49.

TABLE 49.—SENSITIVITY OF MOLYBDENUM REACTIONS

Reagent	Sensitivity in g. of Molybdenum per l.
Potassium ferrocyanide	0.1
Sodium thiosulfate	0.04
Potassium xanthate	0.004
Phenylhydrazine	0.006
Butyl xanthate	0.004
Amyl xanthate	0.004
Pentasol xanthate	0.004
Potassium ethyl xanthate (color extracted with ether)	0.0004
Ammonium thiocyanate-stannous chloride (color extracted with ether)	0.00002

Determination of molybdenum. The red color which is formed by the action of phenylhydrazine upon acid solutions of molybdates may be used for the colorimetric determination of small quantities of molybdenum.[6,8,9] The phenylhydrazine reaction is only approximately one-fourth as delicate as that with potassium thiocyanate and stannous chloride, but the color developed with the former is less sensitive to temperature changes and therefore possesses certain advantages in the colorimetric determination. This method is recommended by Gillis.[87]

The following method has been used by Hauptmann and Balconi[8] for the determination of molybdenum in manganese-iron ore:

Reagent. Add 3 parts of phenylhydrazine and 3 parts of sulfuric acid to 65 parts of water.

Procedure. Grind the ore to a fine powder and dissolve 1 g. in 40 ml. of 1:1 hydrochloric acid. Boil gently until all chlorine is expelled and filter. Wash with hot water and evaporate the filtrate and washings to dryness. Dissolve the residue with 30 ml. of 1:100 hydrochloric acid. Transfer to a 100-ml. flask and add 20 ml. of hot 16 per cent sodium hydroxide solution. Filter through a dry filter and collect 10 ml. of the filtrate for the determination.

To the 10-ml. aliquot, add 5 ml. of the reagent and heat on a water-bath at 80° C. for 15 minutes. If the sample solution is alkaline, add 5 ml. of 10 per cent sulfuric acid. Allow the mixture to stand for 30 minutes and compare with a standard similarly prepared.

Determination of phosphorus. One of the more satisfactory methods for the determination of small quantities of phosphorus is based upon the formation of the phosphomolybdate and subsequent reduction of this compound to a blue product by means of various reducing agents. MacCallum [10] suggested the use of phenylhydrazine for this purpose, and this reaction has subsequently been studied by Taylor and Miller [11] as a means of estimating phosphorus in biological materials. Phosphorus is precipitated as ammonium phosphomolybdate in the usual manner, and from that point the estimation is carried out as follows:

Procedure. Dissolve the washed precipitate of ammonium phosphomolybdate in 5 ml. of 0.1 N sodium hydroxide solution and transfer quantitatively to a 25-ml. flask. In a second flask place 1 ml. of a solution of Na_2HPO_4 containing 0.00026 g. of phosphorus, the amount of molybdate solution containing exactly the corresponding amount of MoO_3, and then 5 ml. of 0.1 N sodium hydroxide solution. To each flask add 2 ml. of a colorless 5 per cent solution of phenylhydrazine hydrochloride, and then to each add 10 ml. of 0.1 N sulfuric acid and dilute to the mark. Mix well and allow the blue color to develop for one-half hour. Compare the resulting colors in a colorimeter.

If the amount of phosphorus in the unknown is very small, the standard phosphorus solution may be diluted with a suitable volume of water.

Terada [12] has used phenylhydrazine for the colorimetric microdetermination of phosphoric acid after precipitating the latter with strychnine molybdate. The precipitate is dissolved in sodium carbonate, and the red color which develops when this solution is heated with phenylhydrazine is compared with standards similarly treated. For the details of this procedure, see section on strychnine.

Alten and coworkers [13] have investigated the method of Terada and have found this to be one of the most satisfactory procedures for determining quantities of phosphorus ranging from 0.05-0.7 mg. of P_2O_5 per 100 ml. of solution. The results are unaffected by less than 8 mg. of citric acid per 100 ml., and quantities of potassium sulfate ranging up to 0.4 g. per 100 ml. do not affect the results.

Detection of silver. Mercurous chloride is slowly reduced to metallic mercury by the action of phenylhydrazine in an acetic acid solution, but this reaction is markedly accelerated by a low concentration of silver ions. This catalytic action has been used by Feigl [14,15,34,35] for the detection of very small quantities of silver.

Procedure. A freshly prepared, thoroughly washed precipitate of mercurous chloride, is suspended in a little water and mixed with a solution consisting of 1 part of phenylhydrazine and 2 parts of acetic acid. Divide this suspension into two parts, and to one add 1 ml. of a dilute solution containing silver ions. A black or gray precipitate of metallic mercury forms immediately (or after a time, depending upon the amount of silver present) if silver ions are present. Reduction is perceptible in the blank test only after a long interval of time. By means of this reaction as little as 0.016γ of silver can be detected in 1 ml. of solution.

Costeanu[16] has used phenylhydrazine for the detection and determination of silver. Filter paper impregnated with an alcoholic solution of phenylhydrazine reduces silver nitrate to metallic silver, which is detected by the appearance of a dark spot on the paper. By comparing the resulting spot with a series of spots formed with solutions of known silver content, the quantity of silver in the unknown may be estimated.

Detection of gold. When a solution of phenylhydrazine acetate is added to a solution containing very small quantities of gold, the mixture appears brown by reflected light and bluish by transmitted light. If an excess of citric acid is first added to the gold solution, and then the phenylhydrazine acetate is added, a violet color appears which remains for several hours.[17,36]

Separation and determination of titanium, zirconium, thorium, aluminum and chromium. Phenylhydrazine may be used to precipitate quantitatively the tetravalent and weakly basic elements titanium, zirconium and thorium (and also aluminum and chromium under suitable conditions) from dilute and slightly acid solutions of the chlorides, sulfates or nitrates of these metals. Ceric and ferric salts are reduced by phenylhydrazine and are precipitated only incompletely, if at all. Zinc, cadmium, mercury, cobalt and nickel when present in sufficient concentration may form difficultly soluble addition products with phenylhydrazine. Magnesium, calcium, strontium, manganese and ferrous iron are not precipitated. This makes possible a number of important separations using phenylhydrazine, such as titanium and zirconium from iron; titanium, zirconium and thorium from beryllium; and aluminum from iron.[18]

A number of procedures have been proposed for the separation of aluminum from iron, manganese, calcium and magnesium.[19-23] Hess and Campbell[19] proposed a satisfactory method for separating aluminum (accompanied by small quantities of phosphorus, titanium and zirconium) from iron and manganese in the presence of small quantities of calcium, magnesium, zinc, nickel, cobalt and copper. This procedure has been modified by Bastos[22] as follows:

Procedure. Dissolve the sample in the usual manner and dilute the resulting solution to 200-300 ml. Heat to boiling and add a dilute solution of ammonium hydroxide as long as the precipitate which forms dissolves readily. Then add a neutral saturated solution of ammonium bisulfite (prepared by passing sulfur dioxide into a cold 1:1 solution of ammonia until the mixture becomes yellow) dropwise with stirring until the solution is colorless. To the hot solution, which smells strongly of sulfur dioxide, add 1-2 ml. of phenylhydrazine. If a permanent precipitate is formed, add a few more drops of the reagent to insure complete precipitation. After all the reagent has been added, heat the solution to boiling and filter immediately. Wash the precipitate, first with a hot 5 per cent solution of ammonium chloride which has been neutralized with ammonium hydroxide to methyl red, and then with hot alcohol, and finally again with ammonium chloride solution. Dissolve the precipitate in 1:1 hydrochloric acid and repeat the precipitation. Dry the precipitate and ignite over a blast lamp to constant weight. The P_2O_5, TiO_2 and ZrO_2 in the precipitate are determined separately and the Al_2O_3 is found by difference.

In a 0.5-g. sample, aluminum is determined with an error of less than 0.5 per cent, provided the oxides precipitated by phenylhydrazine do not exceed 30 per cent.

Boyle and Musser [24] have proposed a modification of the Willard and Tang [25] basic succinate method for the determination of aluminum. In this procedure interference caused by iron is prevented by the use of a few drops of a 10 per cent solution of ammonium bisulfite and 2 ml. of phenylhydrazine. This treatment serves to reduce the iron, and to maintain it in a lower state of oxidation during the precipitation of aluminum as the basic succinate.

According to Dixon [26] phenylhydrazine is not suitable for the separation of beryllium and titanium, since some beryllium is precipitated with the titanium.

In an early study of the use of phenylhydrazine as a precipitant for various metals, Jefferson [27] reported that zirconium was not precipitated, but more recently Allen [18] claims that zirconium is quantitatively precipitated by means of phenylhydrazine if the conditions are properly controlled. This reaction has been used by Ferguson [28] for the precipitation of zirconium in the analysis of ores and alloys. The following procedure is used for the determination of zirconium in steel:

Procedure. Dissolve the steel in hydrochloric and nitric acids. Add 6 ml. of sulfuric acid and evaporate the mixture. Wash the precipitate of silica with hot water, then 1:1 hydrochloric acid, and again with hot water. Treat the residue with sulfuric and hydrofluoric acids, and evaporate to the appearance of sulfur trioxide fumes. Dilute the residue and add to the principal filtrate. Add 6 ml. of ammonium bisulfite solution (see above procedure), cool, neutralize with 1:1 ammonium hydroxide solution, and then acidify with 10 drops of concentrated hydrochloric acid. Then for each 100 ml. of the solution, add 1 ml. of phenylhydrazine and heat to boiling. Allow to stand for 30 minutes, filter, and wash the residue with hot water. Redissolve in hot dilute hydrochloric and sulfuric acids, and reduce the iron with ammonium bisulfite. Neutralize as described above, and again precipitate. By this procedure the zirconium precipitate is free from aluminum and iron.

Results obtained by the above method agree very closely with those using the phosphate method.

Chromium is precipitated quantitatively as chromium hydroxide when neutral or alkaline solutions containing chromates are treated with phenylhydrazine. Thiosemicarbazide, however, is a more satisfactory reagent for this precipitation. The addition of ammonium chloride makes the precipitation more rapid and complete.[29]

Determination of tungsten. When a properly prepared tungstate solution is poured into a hydrochloric acid solution of phenylhydrazine hydrochloride, a flocculent precipitate forms which immediately turns green. This precipitate may be filtered, washed and ignited to WO_3.[30]

Procedure. Pour 50 ml. of a tungstate solution containing 0.004 g. of WO_3 and 2 g. of potassium chloride into a solution of 1 g. of phenylhydrazine in 50 ml. of 8 N hydrochloric acid. Allow to stand for 1 hour on a water-bath. The green needles which form appear to consist of an isomer of yellow WO_3. Wash the precipitate by decantation with a solution containing 5 per cent hydrochloric acid and 1 per cent phenylhydrazine. Then quickly wash onto a filter with hot water to remove most of the reagent. Finally ignite to WO_3.

Detection of ammonia. Diazotized phenylhydrazine reacts with ammonia to give a colored compound which may be used for the detection of small quantities of ammonia. A test paper is prepared by impregnating with the product obtained by diazotizing phenylhydrazine in the usual manner with sodium nitrite in an acid solution. By means of this reagent it is possible to detect a small fraction of a milligram of ammonia in 1 liter of air.[31]

Detection of the platinum metals. Phenylhydrazine hydrochloride and various salts of the platinum metals give reactions which may be used for the microchemical detection of these elements. Results obtained when a solid fragment of phenylhydrazine hydrochloride is added to a 2 per cent solution of the salts of the platinum metals are described in Table 50.[32]

TABLE 50.—REACTIONS OF PLATINUM METALS WITH PHENYLHYDRAZINE HYDROCHLORIDE

Test Material	Description
$RuCl_3$	No apparent reaction.
$RhCl_3$	No apparent reaction.
$PdCl_2$	A brownish-yellow, amorphous precipitate forms around the test particle immediately.
Na_2OsCl_6	No apparent reaction.
$IrCl_4$	The test drop is immediately decolorized in the area surrounding the reagent particle. On standing and as the drop evaporates some small, deep-red octahedra appear near the edge of the drop.
H_2PtCl_6	After standing for some time an extremely scant, very fine, amorphous precipitate forms around the reagent particle.
$AuCl_3$	A dense, blue, amorphous precipitate forms immediately around the reagent particle. Between the precipitate and the edge of the drop many crosses and clusters of irregular, bright-yellow crystals develop.

Determination of selenium. Dolique and coworkers[37] recommend the substitution of phenylhydrazine for sodium bisulfite as a reducing agent for the microdetermination of selenium. According to their procedure, gaseous hydrogen chloride and phenylhydrazine are added to the selenium solution, and the mixture is heated at 70° C. for 7 minutes. Gum arabic is then added to stabilize the selenium sol, and the color is measured in a double photocell photometer. As little as 0.01 mg. of selenium can be determined with an accuracy of 2 per cent.

Detection of carbon disulfide. Liebermann and Seyewetz[33] describe the following test for carbon disulfide in benzene:

Procedure. Add 5 drops of phenylhydrazine to 10 ml. of benzene to be analyzed and allow to stand for 1-2 hours with frequent shaking. A crystalline precipitate forms with as little as 0.03 per cent of carbon disulfide.

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PHENYLHYDRAZINE CINNAMATE

$C_{15}H_{16}O_2N_2$ Mol. Wt. 256.28 Beil. Ref. XV, 111.

$C_6H_5—CH=CH—CO_2H \cdot NH_2—NH—C_6H_5$

Use: Detection of phosgene.

This compound is obtained as colorless needles from water. It melts at 110° C., and is soluble in benzene.

Preparation: Phenylhydrazine cinnamate is prepared by mixing equal quantities of phenylhydrazine and cinnamic acid in benzene. If the mass does not solidify, evaporate the benzene on a water-bath. Purify the salt by crystallizing from boiling water.[1]

Detection of phosgene. Anger and Wang[2] have proposed the use of phenylhydrazine cinnamate for the detection by a spot method of small quantities of phosgene.

Procedure. Place 1 drop of the solution to be tested in a microcrucible, add a small particle of the reagent, and after 5 minutes add 1 drop of 1 per cent copper sulfate solution. Phosgene (carbonyl chloride) reacts with the reagent to form diphenylcarbazide, and this in turn yields a red-violet copper compound. As little as 0.5γ of phosgene can be detected by this method.

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PLASMOCHIN

Synonym: *N*-Diethylaminoisopentyl-8-amino-6-methoxyquinoline

$[(C_2H_5)_2N(CH_2)_3CH(CH_3)NH]CH_3O \cdot C_9H_5N$

Use: Detection of chromium.

Plasmochin is a light yellow almost tasteless powder. It is only slightly soluble in water, but dissolves readily in alcohol.

Preparation: Plasmochin is prepared from diethylaminopentyl chloride hydrochloride and methoxy-8-aminoquinoline. This method, and the preparation of the starting materials, is described by Magidson and Strukow.[1]

Detection of chromium. Chromates and dichromates yield a purple color with plasmochin in the presence of oxalic acid and at a pH of less than 6.5. This color reaction is given at a dilution of 1 part of chromate or dichromate in 100,000 parts of solution. The intensity of the color appears to be proportional to the concentration of the reagent and chromate or dichromate. The complex acids of tungsten and molybdenum give a blue color in an alkaline medium.[2]

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PROPYLAMINE

C_3H_9N Mol. Wt. 59.11 Beil. Ref. IV, 136

$$CH_3—CH_2—CH_2—NH_2$$

Use: Detection of cyanide.

Propylamine is a colorless alkaline liquid having a strong ammoniacal odor. It boils at 48-49° C. and has a sp. gr. of 0.719. It is miscible with water, alcohol and ether. It should be stored in a tightly closed container.

Preparation: Propylamine is prepared by heating propyl iodide in a sealed tube with alcoholic ammonia,[1] or by reducing ethyl cyanide with sodium in alcohol.

Detection of cyanide. Propylamine may be used in place of ammonia with alloxan in the cyanide test used by Kozlovskii and Penner.[2] The amine is used in a 0.1 M solution and is capable of revealing 0.3γ of hydrogen cyanide at a dilution of 1:400,000. This base is one of the most satisfactory of those tried.

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PROPYLENEDIAMINE

Synonym: 1,2-Diaminopropane

$C_3H_{10}N_2$ Mol. Wt. 74.13 Beil. Ref. IV, 257 (417, 418)

$$CH_3—CH(NH_2)—CH_2(NH_2)$$

Use: Determination of copper, mercury and silver.

Propylenediamine is an extremely hygroscopic, strongly alkaline liquid. It rapidly absorbs moisture to form a hemihydrate. It boils at 119-120° C., and is very soluble in water.

Preparation: Mix ethylene bromide with an excess of alcoholic ammonia and heat for 3-4 days at 100° C. Treat the mixture with an excess of solid potassium hydroxide, and heat on a water bath to remove the alcohol and ammonia. Distill off the propylenediamine and dry with metallic sodium.[1]

Determination of silver. Silver is precipitated quantitatively by treating a neutral solution of silver nitrate with an excess of potassium iodide and a concentrated solution of $[Cupn_2]SO_4$ (pn = propylenediamine). The precipitate is pale violet in color and corresponds to the formula $[AgI_2]_2[Cupn_2]$. It contains 23.07 per cent of silver.[2]

The precipitating reagent is very soluble in water and should be prepared as needed by mixing aqueous solutions containing one part of crystalline copper sulfate with two parts of propylenediamine. Silver is precipitated by adding the freshly prepared, hot reagent solution to the boiling silver solution and allowing to cool. The precipitate is washed with a 1.0 per cent potassium iodide solution containing 0.5 per cent $[Cupn_2]SO_4$, then with alcohol, and finally with ether. The precipitate is dried in vacuum and weighed.

Weakly acid solutions of silver salts are neutralized with ammonia, but strongly acid solutions are evaporated to dryness on a water bath, the residue dissolved in water, and completely neutralized with ammonia. Large quantities of ammonium salts must not be present, since the silver salt is somewhat soluble. For the same reason, a large excess of the reagent must be avoided.

Reagent. Mix an aqueous solution of copper sulfate with propylenediamine hydrate in the ratio of one part of copper sulfate to two parts of propylenediamine.

Procedure. To 50-100 ml. of a neutral or slightly ammoniacal solution of silver nitrate, containing 1-4 mg. of silver, add an excess of potassium iodide until solution is complete, and then heat to boiling. Mix with a freshly prepared, hot, concentrated solution of copper propylenediamine sulfate. Filter through a filter crucible, and wash with a 1 per cent potassium iodide solution containing 0.5 per cent copper propylenediamine sulfate, and then 3-4 times with 1-2 ml. alcohol and also 3-4 times with 1-2 ml. of ether. Dry 10 minutes in a vacuum desiccator and weigh. The factor for silver is 0.2307.

Determination of mercury. An insoluble bluish-violet complex of $[Cupn_2][HgI_4]$ is formed when a concentrated solution of $[Cupn_2]SO_4$ is added to a solution of a mercuric salt containing an excess of potassium iodide. This reaction may be used for the gravimetric determination of mercury.[3]

Reagent. Copper propylenediamine sulfate, $[Cupn_2]SO_4$, is used as the reagent, and should be prepared as needed by mixing aqueous solutions containing one part of crystalline copper sulfate with two parts of propylenediamine.

Procedure. To 100-250 ml. of a neutral or faintly ammoniacal solution of mercuric salt, add an excess of potassium iodide, and heat the mixture nearly to boiling. Add an excess of a boiling-hot concentrated solution of $[Cupn_2]SO_4$. Cool, filter through a porcelain filtering crucible, and wash the precipitate three or four times with a solution containing 0.1 per cent potassium iodide and 0.1 per cent $[Cupn_2]SO_4$, then three or four times with 2-ml. portions of 96 per cent alcohol, and finally two to four times with 2-ml. portions of ether. Dry in a vacuum desiccator and weigh. The factor for mercury is 0.2181.

This method for determining mercury is simple and accurate, even in the presence of considerable quantities of ammonia, copper, cobalt, chromium, nickel and zinc salts.

Sandin and Margolis [4] have used the above method for the determination of mercury in iodinated organic compounds of mercury.

Determination of copper. Copper can be determined by modifying the above procedure, using propylenediamine and the complex mercuric iodide ion as the precipitant.[3]

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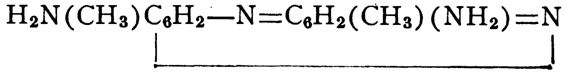
SAFRANINE

Synonym: 3,6-Diamino-2,7-dimethylphenazine

$C_{14}H_{14}N_4$ Mol. Wt. 238.25 Beil. Ref. XXV, 403 (657)



$$H_2N(CH_3)C_6H_2—N=C_6H_2(CH_3)(NH_2)=N$$

Use: Detection of nitrate, nitrite, and rhenium.

Determination of nitrate.

Safranine is a reddish-brown powder. It dissolves in water to form a red colored solution. It also dissolves in concentrated sulfuric acid to give a green color, and upon dilution first turns blue and then violet. Safranine of commerce is a mixture of 10-phenyl-3,6-diamino-2,7-dimethylphenazinium hydrochloride, the 10-*o*-tolyl compound and other homologs and isomers.

Preparation: Treat *o*-toluidine with nitrous acid to form 5-*o*-tolueneazo-2-aminotoluene, then reduce with zinc or powdered iron and hydrochloric acid, and oxidize the mixture of *p*-toluylenediamine and *o*-toluidine in the presence of aniline with potassium dichromate.[1-3]

Detection of nitrite. Eegriwe [4,7] has used safranine for the detection of nitrite:

Procedure. Add 1 drop of 0.03 per cent safranine solution for each ml. of the acid solution to be tested and 1 ml. of 2 N sulfuric acid for each ml. of the neutral or alkaline solution to be tested. A blue coloration is observed if 0.02 mg. of nitrite is present in 5 ml. of the solution. A reddish-violet color appears if only 0.001 mg. of nitrite is present in 5 ml. The color is due to the formation of monodiazosafranine.

Nitrate interferes with the nitrite test by forming a crystalline precipitate. Nitrate may be detected by the nitrite reaction after a preliminary reduction with powdered magnesium.

Determination of nitrate. Vasil'ev and Dukhinova [5] use safranine to facilitate the visual evaluation of the color obtained in the colorimetric determination of nitrate with *β*-methylumbelliferone.

Detection of rhenium. Safranine forms an insoluble perrhenate and chlororhenate.[6]

1. A. W. Hoffmann and A. Geyger, *Ber.* **5**, 527 (1872).
2. H. R. Bindschedler, *Ber.* **13**, 207 (1880).
3. O. N. Witt, *Ber.* **10**, 874 (1877).
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5. A. S. Vasil'ev and M. M. Dukhinova, *Zavodskaya Lab.* **10**, 35-7 (1941); *C.A.* **35**, 5061 (1941).
6. L. C. Hurd, *Ind. Eng. Chem., Anal. Ed.* **8**, 11-15 (1936); *C.A.* **30**, 1325 (1936).
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SEMICARBAZIDE HYDROCHLORIDE

Synonym: Aminourea hydrochloride

$CH_5ON_3 \cdot HCl$ Mol. Wt. 111.54 Beil. Ref. III, 100

$$H_2N—CO—NH—NH_2 \cdot HCl$$

Use: Detection of cyanate, gold, iridium, palladium and platinum.

Determination of cyanate.

Semicarbazide hydrochloride is a yellowish-white crystalline solid. It melts at 173° C. with decomposition. It is soluble in water, but is insoluble in absolute alcohol and ether.

Preparation: Dissolve 52 g. of hydrazine sulfate and 21 g. of anhydrous sodium carbonate in 200 ml. of boiling water and cool the solution to 50° C. Then add a solution of 35 g. of potassium cyanate in 100 ml. of water and allow the mixture to stand overnight. Add 60 ml. of acetone and again allow to stand, with frequent shaking, for 24 hours. Filter off the acetone semicarbazone which separates from the liquid, and evaporate the mother-liquor to dryness on a water-bath. Extract the powdered residue with alcohol in an extraction apparatus Semicarbazone crystallizes in the flask of the apparatus. Decompose the semicarbazone by warming gently with concentrated hydrochloric acid, which is added in the ratio of 8 ml. of acid for each 10 g. of the material. Continue heating until solution is just complete, and then allow to cool. Semicarbazide hydrochloride separates as a thick crystalline mass. Filter with suction and wash first with a little cold 1:1 hydrochloric acid and then twice with 3-5 ml. portions of ice cold alcohol. Dry in a desiccator.[1,2]

Detection and determination of cyanate. Cyanates may be detected by a reaction based on the formation of a precipitate of hydrazodicarbamide, $NH_2—CO—NH—NH—CO—NH_2$, when a solution of a cyanate reacts with a solution of semicarbazide hydrochloride. The solubility of the reaction product in water is 1 part in 6666. The reaction is carried out as follows:[3]

Procedure. To a solution containing the equivalent of 0.2-0.5 g. of potassium cyanate in about 20 ml. of water, add 1 g. of 98 per cent semicarbazide hydrochloride and allow to stand for 24 hours. Filter and wash with 10 ml. of water saturated with hydrazodicarbamide. Dry the precipitate at 100° C., cool and weigh.

Reactions of the platinum metals. Whitmore and Schneider[4] have investigated the use of semicarbazide hydrochloride as a microchemical reagent for the platinum metals. Palladium yields many short, slender, pale yellow prisms. Iridium chloride also yields pale, yellow prisms when the reaction mixture is allowed to stand. On standing for some time as the drop of the reaction mixture evaporates, a few extremely small bright-yellow octahedra develop around the edge of a drop containing chloroplatinic acid. Gold chloride yields a blue amorphous precipitate immediately.

1. J. Thiele and O. Stange, *Ber.* **27**, 31 (1894).
2. H. Biltz, *Ann.* **339**, 250 (1905).
3. J. Leboucq, *J. pharm. chim.* **5**, 531-9 (1927); *C.A.* **21**, 3174 (1927).
4. W. F. Whitmore and H. Schneider, *Mikrochemie.* 17, 279-319 (1935).

SULFANILAMIDE

Synonym: *p*-Aminobenzenesulfonamide

$C_6H_8O_2N_2S$ Mol. Wt. 172.20 Beil. Ref. XIV, 698.

$$H_2N—C_6H_4—SO_2NH_2$$

Use: Determination of nitrite.

Sulfanilamide is a white crystalline solid. It is odorless and neutral in reaction. It melts at 164.5-166.5° C. It is only slightly soluble in water but is more soluble in alcohol and acetone. It is very soluble in boiling water and in hydrochloric acid. It is also soluble in solutions of sodium or potassium hydroxide.

Preparation: *p-Acetamidobenzenesulfonyl chloride.* Place 20 ml. of chlorosulfonic acid in a *dry* 50-ml. Erlenmeyer flask and cool to 10-15° C. Do not cool below 10° C. Add 7 g. of finely powdered *dry* acetanilide in small portions and with thorough mixing so that the temperature does not rise above 20° C. When the solid has dissolved, immerse the flask in a beaker containing just enough water to come to the level of the reaction mixture in the flask. Heat the water to 60-70° C. for one hour, keeping the water level the same as that of the liquid in the flask.

Pour the reaction mixture slowly onto a well-stirred mixture of 150 g. of finely cracked ice and a little water. Break up any lumps which have formed and filter on a Buchner funnel. Wash several times with cold water, and remove as much water as possible with suction.

p-Acetamidobenzenesulfonamide. Place the product obtained above in a 100-ml. Erlenmeyer flask, and add 25 ml. of concentrated ammonium hydroxide. Stir the mixture with a glass rod until a smooth paste is obtained, and then heat at 70° C. for 30 minutes. Cool the mixture by placing the flask in an ice-bath, and acidify the mixture with dilute sulfuric acid to Congo red. Cool thoroughly in the ice-bath, and filter through a Buchner funnel. Wash with cold water and dry.

Sulfanilamide. Place the dry product obtained in the last step in a 50-ml. Erlenmeyer flask, and add 1:2 hydrochloric acid in the ratio of 2 ml. of acid for each gram of the *p*-acetamidobenzenesulfonamide. Boil with reflux for one hour and pour the solution into a 100-ml. Erlenmeyer flask and dilute with an equal volume of water. Add a little decolorizing charcoal, heat to boiling and filter into a clean 600-ml. beaker. Add solid sodium carbonate with continuous stirring until the solution is just alkaline to litmus. Cool thoroughly in an ice-bath, and filter with suction. Wash with cold water and dry.

Purify by recrystallizing from water. Use 12 ml. of water for each 1.0 g. of sulfanilamide. Add a little decolorizing charcoal to the hot solution, boil for a few minutes, filter, and allow to cool. Sulfanilamide separates from the filtrate as a white crystalline solid.[1]

Determination of nitrites. Sulfanilamide has been used with N-(1-naphthyl)-ethylenediamine dihydrochloride in place of sulfanilic acid and α-naphthylamine in the well-known reaction for nitrites.[2] Sulfanilamide may be obtained in a high state of purity, is more stable than sulfanilic acid, and reacts more rapidly in the coupling process. Sulfanilamide may also be used as a primary nitrite standard in the nitrite determination.

The following procedure, which is taken directly from the published work of Shinn,[2] may be used for the determination: *

Reagent. Dissolve 0.2 g. of sulfanilamide in 100 ml. of distilled water. This solution will keep for one month in a refrigerator. Winthrop's "prontylin, sulfanilamide powder repurified for injection," may be used.

N-(1-naphthyl)-ethylenediamine dihydrochloride solution. Dissolve 0.1 g. of the of the N-(1-naphthyl)-ethylenediamine dihydrochloride in 100 ml. of distilled water. Store in a dark bottle. This solution is referred to in the following discussion as the "coupling agent."

Ammonium sulfamate solution. This is a 0.5 per cent solution of the reagent in water.

Standardization of sulfanilamide solution. Dry analytical reagent grade sodium nitrite for 24 hours in a desiccator. Dilute a weighed sample of about 1 gram to 100 ml. in a volumetric flask and assay by titration with potassium permanganate according to the U.S.P. XI method.

A. Employing the assayed sodium nitrite, prepare an accurately known solution containing about 0.005 mg. of nitrite per ml. With a transfer pipet measure 5 ml. of this into each of two 50-ml. volumetric flasks, add 1 ml. of 50 per cent hydrochloric acid and 5 ml. of the 0.2 per cent sulfanilamide solution, and after 3 minutes add 1 ml. of the ammonium sulfamate reagent. (The sulfamate plays no part here but is added to ensure uniformity of treatment.) Two minutes later add 1 ml. of the coupling agent and dilute to volume with water.

B. At the same time into two other 50-ml. volumetric flasks measure 5 ml. of an accurately prepared 1:100 dilution of the 0.2 per cent sulfanilamide solution. Add 1 ml. of 50 per cent hydrochloric acid, 1 ml. of 0.1 per cent sodium nitrite, and about 5 ml. of water. Allow to stand 3 minutes, add 1 ml. of ammonium sulfamate solution to destroy excess nitrite, let stand 3 minutes, add 1 ml. of the coupling agent, and dilute to volume.

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Samples A and B prepared as above are read against each other in a colorimeter. With a Duboscq-type colorimeter the nitrite equivalent value of the sulfanilamide solution is calculated from the equation:

$$\frac{\text{Reading of } A}{\text{Reading of } B} \times \text{mg. of } NO_2^- \text{ in } A \times 20 = \text{mg. of } NO_2^- \text{ represented by}$$
$$\text{1 ml. of 0.2 per cent sulfanilamide solution.}$$

Procedure. The solution taken for analysis should be either neutral or acid. Variations in acid concentration between 0.1 and 1 N at the time of coupling do not influence the final color. The unknown should contain no more than 0.05 mg. of nitrite and should be limited in volume to no more than 35 ml. To the unknown sample add 1 ml. of 50 per cent hydrochloric acid, 5 ml. of 0.2 per cent sulfanilamide solution, and let stand for 3 minutes. Add 1 ml. of ammonium sulfamate solution. After 2 minutes add 1 ml. of coupling reagent and dilute to volume. At the same time prepare a nitrite standard from the sulfanilamide solution according to the procedure outlined in B. The unknown is read against the standard and the nitrite present in the sample taken is calculated by the equation:

$$\frac{\text{Reading of standard}}{\text{Reading of unknown}} \times \frac{NO_2^- \text{ value of 1 ml. 0.2\% sulfanilamide}}{20}$$
$$= \text{mg. of } NO_2^- \text{ in sample.}$$

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2. M. B. Shinn, *Ind. Eng. Chem., Anal. Ed.* 13, 33-5 (1941); *C.A.* 35, 1352 (1941).

SULFANILIC ACID

Synonym: Aminosulfonic acid, *p*-aminobenzenesulfonic acid

$C_6H_7O_3NS$ Mol. Wt. 173.18 Beil. Ref. XIV, 695.

$HO_3S—C_6H_4—NH_2$

Use: Detection of ammonia, cerium and nitrite.

Determination of aluminum, iodide, iodine, magnesium, nitrite, potassium and sodium.

Sulfanilic acid is a white crystalline solid. It occurs as the monohydrate, but becomes anhydrous on heating to 100° C. It chars at 280-300° C. without melting. It dissolves slowly in about 90 parts of cold water or 15 parts of boiling water, and is almost insoluble in alcohol, benzene and ether.

Preparation: Mix gradually 100 g. of pure concentrated sulfuric acid and 31 g. of aniline in a dry flask with shaking. Heat the mixture in an oil bath at 180-190° C. for 4 or 5 hours, or until aniline is no longer liberated when sodium hydroxide is added to a little of the diluted sample. Cool the reaction mixture somewhat, and then pour with stirring into cold water. Filter with suction, wash the crystals with water, and then recrystallize from water containing a little animal charcoal.

Detection and determination of nitrite. Sulfanilic acid is most frequently used as an analytical reagent for the detection and determination of nitrites. In conjunction with α-naphthylamine it yields a red coloration. This reaction, and the references to its use, are discussed in the section on α-naphthylamine (pages 404-406). Sulfanilic acid has also been used with other coupling agents for the detection and determination of nitrites. Zambelli,[1] for example, has recommended the use of α-naphthol and phenol and Erdmann [2] has used 8-amino-8-hydroxynaphthalene-4,6-disulfonic acid.

Determination of potassium. Sulfanilic acid is used indirectly in a number of procedures for determining potassium after a preliminary separation as the cobaltinitrite. According to Alten and co-workers,[3] the most satisfactory method for developing the color of the nitrite is with sulfanilic acid and α-naphthylamine. For details of this procedure, see section on α-naphthylamine (page 408). Rozanov and Kazarinova [4] have used a similar reaction in which phenol is used as the coupling agent.

Determination of sodium. Sodium may be separated from potassium and other metals with which it is commonly associated by precipitation as the complex sodium cesium bismuth nitrite, $6NaNO_2\cdot9CsNO_2\cdot5Bi(NO_2)_3$.[5] This salt may be dissolved and the sodium indirectly determined by developing the red color caused by nitrites with sulfanilic acid and α-naphthylamine.[6] For details of this procedure, see section on α-naphthylamine (page 408).

Determination of magnesium. Magnesium is determined colorimetrically by a procedure based on the following steps: Precipitate magnesium with 8-hydroxyquinoline, dissolve the precipitate in hydrochloric acid and couple with diazobenzenesulfonic acid, which is formed by the diazotization of sulfanilic acid. The amount of magnesium present in the hydroxyquinoline is estimated from the color of the resulting solution.[7] For details, see section on 8-hydroxyquinoline.

Determination of aluminum. Like magnesium, aluminum forms with 8-hydroxyquinoline a precipitate which may be coupled with a diazo compound in an alkaline solution to form a yellowish-red dye which is suitable for colorimetric estimation.[8] For details of this procedure, see section on 8-hydroxyquinoline.

Detection of ammonia. Diazotized sulfanilic acid reacts with ammonia to give a colored compound which may be used for the detection of ammonia.[9] By treating sulfanilic acid with sodium nitrite and hydrochloric acid, a test paper is prepared with which it is possible to detect a fracton of a milligram of ammonia in 1 liter of air.

Detection of cerium. A reagent consisting of 0.5 g. of sulfanilic acid and 5 ml. of sulfuric acid in 100 ml. of water gives a blood-red color with ceric salts.[10] This test is sensitive to 20 mg. of cerium per liter of solution. Wenger and Duckert[11] do not recommend this reaction, since it is similar to that obtained with zirconium and thorium.

Determination of iodine and iodides. Iodine oxidizes hydroxylamine to nitrous acid, which is capable of converting sulfanilic acid to a diazonium salt. This may be coupled with α-naphthylamine to produce a red dye which can be estimated colorimetrically by any of the usual methods.[12] Thus, by adding an excess of hydroxylamine to a solution containing free iodine and then treating with sulfanilic acid and α-naphthylamine, iodine may be indirectly estimated. For the details of this procedure, see section on α-naphthylamine (page 411).

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4. S. N. Rozanov and V. A. Kazarinova, *Z. anal. Chem.* **96**, 26-9 (1934); *C.A.* **28**, 1951 (1934).
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6. E. A. Doisy and R. D. Bell, *J. Biol. Chem.* **45**, 313-23 (1920-21).
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11. P. Wenger, R. Duckert and Y. Rusconi, *Helv. Chim. Acta.* **25**, 1547-52 (1942).
12. G. Endres and L. Kaufman, *Z. physiol. Chem.* **243**, 144-8 (1936); *C.A.* **31**, 67 (1937).

TETRAMETHYL-4,4′-DIAMINOBENZOPHENONE

Synonym: Michler's ketone

$C_{17}H_{20}ON_2$ Mol. Wt. 268.35 Beil. Ref. XIV, 89.

$$(H_3C)_2N—C_6H_4—CO—C_6H_4—N(CH_3)_2$$

Use: Determination of tungsten.

Tetramethyl-4,4′-diaminobenzophenone consists of white to greenish leaflets. It melts at 172-172.5° C. It boils above 360° C. with decomposition. It is insoluble in water, very slightly soluble in ether, but dissolves in alcohol and warm benzene.

Preparation: To a weighed quantity of dimethylaniline, at ordinary temperature and with frequent shaking, add phosgene until the theoretical quantity is indicated by the increase in weight of the solution. The compounds react in the ratio of 2 moles of dimethylaniline to 1 mole of phosgene. Boil the mixture with water to remove the excess of dimethylaniline and rapidly dissolve in hydrochloric acid. Precipitate with sodium hydroxide until the base is obtained as a yellow crystalline compound. Crystallize from alcohol and wash with cold alcohol or water.[1,2]

Precipitation of tungstic acid. Tungstic acid may be precipitated with tetramethyl-4,4′-diaminobenzophenone by a procedure proposed by Kafka:[3]

Reagent. Dissolve 7.5 g. of tetramethyl-4,4′-diaminobenzophenone in 10 ml. of concentrated hydrochloric acid and dilute with water to 100 ml.

Procedure. To about 50 ml. of solution containing 0.25 mg. of sodium tungstate, add 10 ml. of the reagent solution. Tungsten is precipitated as a dark brown compound which becomes scarlet-red on drying. This compound has a composition corresponding to $2WO_3 \cdot 3C_{17}H_{20}N_2O$. This contains 36.59 per cent WO_3. The precipitate is filtered with suction, washed free of chloride with a solution prepared by dissolving 5 g. of the reagent in 100 ml. of water and dried and ignited to tungstic oxide.

This procedure seems to offer no advantages over the better-known methods.

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2. W. Michler, *Ber.* 9, 1900 (1876).
3. E. Kafka, *Z. anal. Chem.* **52**, 601-6 (1913); *C.A.* **7**, 3939 (1913).

TETRAMETHYL-*p*-PHENYLENEDIAMINE

Synonym: Wurster's reagent

$C_{10}H_{16}N_2$ Mol. Wt. 164.24 Beil. Ref. XIII, 74.

$$(CH_3)_2N—C_6H_4—N(CH_3)_2$$

Use: Detection of copper, hydrogen cyanide, hydrogen peroxide, iron, mercury, osmium, oxidizing agents, ozone and silver.

Tetramethyl-*p*-phenylenediamine is a white crystalline solid which melts at 51° C. and boils at 260° C. It is slightly soluble in cold water but is more soluble in hot water. It dissolves freely in alcohol, ether and chloroform.

Preparation: Place 20 g. of *p*-phenylenediamine hydrochloride (for preparation, see page 436) and 20 g. of methyl alcohol in a sealed tube and during a period of 2 hours gradually heat the mixture to 170-80° C. Keep at this temperature for about 6-7 hours, and finally during a period of 1 hour increase the temperature to 200° C. Open the tube and transfer the contents to an evaporating dish with the aid of methyl alcohol and evaporate to dryness on a water-bath. Mix the residue with an excess of concentrated sodium hydroxide and allow to stand for a short time, and then filter off the base through glass wool. Wash the residue with a little cold water, dry on a porous plate and distill. The base is obtained as a yellow crystalline mass. Purify by recrystallizing two times from petroleum ether.[1,2]

Detection of copper, silver, mercury and iron. Tetramethyl-*p*-phenylenediamine in an acetone solution is oxidized to a violet colored compound by means of cupric, silver, mercurous, mercuric and ferric ions. Kul'berg[3] has used this reaction for the detection of the above mentioned ions. The test is carried out by adding 1 drop of a solution of 20 mg. of tetramethyl-*p*-phenylenediamine in 100 ml. of acetone to 1 drop of the solution to be tested. The sensitiveness of these reactions is given in Table 51.

TABLE 51.—REACTIONS OF CATIONS WITH TETRAMETHYL-*p*-PHENYLENEDIAMINE

Ion	Sensitivity
Cupric	0.08γ
Silver	0.01γ
Mercuric	1.00γ
Mercurous	0.50γ
Ferric	1.20γ

Detection of osmium. Osmium may be detected by the oxidizing action of osmic acid upon an acetone solution of tetramethyl-*p*-phenylenediamine.[4]

Procedure. Heat 0.8 ml. of an acetate buffer of pH 4.0 and 0.1 ml. of a 0.05 per cent solution of tetramethyl-*p*-phenylenediamine in acetone for 15 minutes with 0.1 ml. of the solution to be tested. As little as 0.005γ of osmium can be detected by the color which forms.

Detection of hydrogen cyanide. Hydrogen cyanide may be detected by immersing a strip of filter paper in a solution of tetramethyl-*p*-phenylenediamine and allowing to dry, and then moistening with copper sulfate and suspending in a bottle containing the gas to be tested. A Burgundy-red color appears if hydrogen cyanide is present.[5]

Detection of ozone and hydrogen peroxide. Wurster[6] observed that tetramethyl-*p*-phenylenediamine is colored blue by hydrogen peroxide and ozone. This reaction has been used for the detection of ozone.[7] Arnold and Mentzel,[8] however, report that this reaction is not useful in characterizing ozone, since aqueous solutions of the reagent also turn blue with chlorine, bromine and nitrogen dioxide, and a similar reaction is obtained with hydrogen peroxide. Eschbaum[9,10] has used the following reaction to detect ozone in water.

Procedure. Dissolve 1 g. of tetramethyl-*p*-phenylenediamine in 100 ml. of hot water and add 20 drops of glacial acetic acid, and finally decolorize the solution with zinc dust. Water containing ozone is immediately colored deep blue with this reagent.

Hydrogen peroxide gives this reaction immediately only after the addition of ferrous sulfate.

1. R. Meyer, *Ber.* **36**, 2979 (1903).
2. C. Wurster, *Ber.* 12, 526 (1879).
3. L. M. Kul'berg, *J. Applied Chem.* (*U.S.S.R.*). **10**, 567-9 (1937) ; *C.A.* 31, 6129 (1937).
4. L. M. Kul'berg, *J. Gen. Chem.* (*U.S.S.R.*). 8, 1139-42 (1938) ; *C.A.* **33**, 4899 (1939).
5. J. Peset and J. Aguilar, *Arch. med. legal* (*Portuguese*). 1, 18-21 (1922) ; *C.A.* **17**, 3149 (1923).
6. C. Wurster, *Ber.* 19, 3195 (1886) ; **21**, 921 (1888).
7. L. M. Kul'berg, *J. Applied Chem.* (*U.S.S.R.*). **10**, 569 (1937).
8. C. Arnold and C. Mentzel, *Ber.* **35**, 1324 (1902).
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10. F, Eschbaum, *Pharm. Zentralhalle.* 38, 133 (1897).

N,N′-TETRAMETHYL-*o*-TOLIDINE

Synonym: Tetron

$C_{18}H_{24}N_2$ Mol. Wt. 254.37 Beil. Ref. XIII, 258(79).

$(CH_3)_2N—(CH_3)C_6H_3—C_6H_3(CH_3)—N(CH_3)_2$

Use: Detection and determination of rhenium.

Tetron crystallizes as leaves from alcohol. It melts at 78° C. It is insoluble in water but dissolves readily in hot alcohol and ether.

Preparation: Tetron is prepared by warming *o*-tolidine with 5 moles of methyl iodide in an aqueous sodium carbonate solution under reflux and on a water-bath. The mixture is warmed until the methyl iodide disappears. On cooling an oily layer separates which eventually solidifies. Filter, while warm, wash with warm water and crystallize from alcohol.[1,2]

Detection and determination of rhenium. Hydrochlororhenic acid, H_2ReCl_6 reacts with tetron to form characteristic crystals that may be used for the microchemical detection of rhenium. For the identification of $HReCl_4$ and H_2ReCl_6 in the presence of one another, the crystals obtained with tetron may be used, although the method is not entirely satisfactory.[3-5]

Tetron is an excellent precipitant for hydrochlororhenic acid, but does not precipitate perrhenic acid $HReO_4$. This reaction may be used for the determination of hydrochlororhenic acid.[4]

Procedure. Heat to 40-50° C. 25-30 ml. of a solution containing 0.3-0.45 mg. of H_2ReCl_6 in the presence of H_2ReO_4 and a little hydrochloric acid. Add dropwise and with vigorous stirring, a slight excess of a solution prepared by dissolving 5 g. of tetron in 100 ml. of dilute hydrochloric or sulfuric acid. After complete precipitation, the solution should contain about 0.2-0.4 g. of tetron in excess. Allow to stand 20-30 minutes, then cool in ice water for 30-60 minutes and filter. Wash the precipitate, first with a 0.1 per cent solution of tetron and then with a little ice water. Dry at 110-130° C. and weigh. The factor for rhenium is 0.2784.

Perrhenic acid may be determined in the filtrate by precipitating as nitron perrhenate.

1. W. Michler and A. Sampaio, *Ber.* **14**, 2170 (1881).
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3. W. Geilmann and F. W. Wrigge, *Z. anorg. allgem. Chem.* **231**, 66-77 (1937); *C.A.* **31**, 3415 (1937).
4. W. Geilmann and L. C. Hurd, *Z. anorg. allgem. Chem.* **213**, 336-42 (1933); *C.A.* **27**, 5026 (1933).
5. C. Hurd, *Ind. Eng. Chem., Anal. Ed.* **8**, 11-15 (1936); *C.A.* **30**, 1325 (1936).

o-TOLIDINE

Synonym: 3,3′-Dimethylbenzidine

$C_{14}H_{16}N_2$ Mol. Wt. 212.28 Beil. Ref. XIII, 256.

$H_2N—(CH_3)C_6H_3—C_6H_3(CH_3)—NH_2$

Use: Detection of cerium, chlorine, chromium, cobalt, copper, gold, hydrogen cyanide, hydrogen peroxide, iodate, iodide, iridium, iron, lead, manganese, mercury, nitrate, nitrite, osmium, palladium, platinum, rhodium, ruthenium, silver, sulfur chlorides, thallium, thiocyanate and vanadium.

Determination of chlorine, cobalt, copper, gold, iodate, iodide, lead, manganese, mercury, nitrate, nitrite, oxygen, silver, sulfate and tungsten.

o-Tolidine consists of white to reddish crystals or crystalline powder. It melts at 129-30° C. It is only slightly soluble in water, but is soluble in alcohol, ether and dilute acids. It should be stored in a well-stoppered bottle and protected from light.

Preparation: *Hydrazotoluene:* Place 100 g. of distilled *o*-nitrotoluene (containing not more than 4 per cent *p*-nitrotoluene), 100 g. of 30 per cent sodium hydroxide solution and 100 ml. of water in a beaker. Arrange to stir mechanically, and heat to 95° C. Remove the source of heat, and add with stirring a few grams of zinc dust. The heat of reaction causes the temperature to rise to 100° C. When the temperature falls to 98° C., add a few more grams of zinc dust, and again allow the temperature to fall to 98° C. before further addition of zinc.

During the reduction, remove small samples of the reaction mixture with the aid of a stirring rod. At first, yellowish-red crystals form on the rod, then a red crystalline solid, and finally a lemon-yellow crystalline product. At this point, discontinue the addition of zinc. Approximately 160 g. of zinc dust is required for the reduction. After all zinc has been added, allow the reaction to run an additional 30 minutes with heating.

Cool the mixture quickly by adding a large volume of cold water with stirring. When the temperature falls to 30° C., pour the mixture into a large beaker, and add a large quantity of ice. Then add concentrated hydrochloric acid with stirring until the mixture is acid to Congo red. Add the acid at such rate that the temperature does not exceed 5° C. Filter off the hydrazotoluene and wash with cold water.

o-Tolidine: Boil the hydrazotoluene slowly with 500 ml. of water and 120 ml. of concentrated hydrochloric acid. Filter and add a saturated solution of sodium sulfate until tolidine sulfate is completely precipitated. Filter, and wash the precipitate with warm water until free of acid. Heat the moist product to 50° C. with a little water, and add a 30 per cent sodium hydroxide solution with stirring until the mixture is alkaline to phenolphthalein. Allow to cool. Filter off the free base and dry at 50° C. Crystallize from benzene or alcohol, or from hot (not boiling) water.[70,71]

Analytical use of *o*-tolidine. *o*-Tolidine is similar to benzidine in reactions used for the detection and determination of many cations and anions, but it appears from a review of the existing data on both reagents, that a greater accuracy and sensitivity can be obtained with *o*-tolidine.[2]

Detection and determination of chlorine. *o*-Tolidine reacts in acid solutions with free chlorine to yield a yellow to orange colored product. This reaction is very sensitive and may be used for the detection and determination of small quantities of free chlorine.[3,4] This reaction is not specific for chlorine, but is given by many substances.

The color formation is based upon an oxidation-reduction reaction, so that oxidizing agents, reducible substances and unstable chlorine addition products behave similarly. Ferric compounds,[3,5-7] manganic compounds,[8-10] organic iron compounds,[11] lignocellulose [11] and algae are among the materials which may cause a color similar to, or affect the color produced by free chlorine. It is possible, after applying the *o*-tolidine test, to report free chlorine in samples where none actually exists, due to the presence of oxidizing impurities.

The most important application of the *o*-tolidine reaction for chlorine is for the determination of chlorine in chlorinated waters; hence, in many cases substances which normally would interfere are absent or are present in such small quantity that no confusion arises. For example, in chlorinated waters containing less than 0.3 p.p.m. of iron, 0.01 p.p.m. of manganic manganese and/or 0.3 p.p.m. of nitrogen as nitrite, the development of the characteristic yellow color with *o*-tolidine may be regarded as due to residual or free chlorine.[12]

Suspended matter may interefere, as is true of all colorimetric determinations, but this may be eliminated by centrifuging the test solution before the determination is carried out. If chloramines are present, as when the ammonia treatment is used, the *o*-tolidine method determines both the free chlorine and the chlorine present in the chloramine.

The color obtained in the chlorine-*o*-tolidine reaction is not very stable and fades after a short time. At the end of an hour, for example, the color fades to approximately 50 per cent of its original intensity.

A standard solution of chlorine is not satisfactory for comparison processes, since results obtained by this method are not consistent unless great care is exercised. A much more satisfactory procedure is to prepare permanent standards from potassium dichromate and copper sulfate.[9]

If not more than 0.3 p.p.m. of iron, 0.01 p.p.m. of manganic manganese and/or 0.3 p.p.m. of nitrite nitrogen is present, free chlorine in water may be determined by the following procedure:

Reagents. *o-Tolidine reagent:* Dissolve 1 g. of *o*-tolidine (M.P. 129° C.) as follows: Place 1 g. of *o*-tolidine in a six-inch mortar and add 5 ml. of hydrochloric acid solution prepared by adding 100 ml. of the concentrated acid to 400 ml. of distilled water. Grind to a thin paste and add 150-200 ml. of distilled water. Transfer the solution to a 1000-ml. graduate and dilute to 505 ml. with distilled water. Finally dilute to 1 liter by adding the remainder of the diluted hydrochloric acid prepared as described above.

Store this solution in amber bottles and do not use after six months. It should not be heated to high temperatures, and should not stand in direct sunlight.[13] After the solution becomes cold, *o*-tolidine hydrochloride crystals may separate.

Standard solution: (a) *Copper sulfate solution:* Dissolve 1.5 g. of copper sulfate ($CuSO_4 \cdot 5H_2O$) and 1 ml. of concentrated sulfuric acid in distilled water and dilute to 100 ml.

(b) *Potassium dichromate solution:* Dissolve 0.25 g. of potassium dichromate ($K_2Cr_2O_7$) and 1 ml. of concentrated sulfuric acid in distilled water and dilute to 1 liter.

When the color comparison is made in 100-ml. Nessler tubes, having the graduation mark 300 mm. from the bottom, use standards prepared according to Table 52.

TABLE 52.—STANDARDS FOR DETERMINATION OF CHLORINE WITH *o*-TOLIDINE

Chlorine p.p.m.	Copper Sulfate Solution ml.	Potassium Dichromate ml.
0.01	0.0	0.8
0.02	0.0	2.1
0.03	0.0	3.2
0.04	0.0	4.3
0.05	0.4	5.5
0.06	0.8	6.6
0.07	1.2	7.5
0.08	1.5	8.2
0.09	1.7	9.0
0.10	1.8	10.0
0.20	1.9	20.0
0.25	1.9	25.0
0.30	1.9	30.0
0.35	1.9	34.0
0.40	2.0	38.0
0.50	2.0	45.0
0.60	2.0	51.0
0.70	2.0	58.0
0.80	2.0	63.0
0.90	2.0	67.0
1.00	2.0	72.0

After mixing the proper quantities of the copper sulfate and potassium dichromate solutions, dilute with distilled water to 100 ml.

Standards prepared according to the above directions are not to be used when the depth of the solution is less than 300 mm. The depth of the liquid should be 300 mm., plus or minus 6 mm.

If the 100-ml. comparison tubes have the graduation mark 240 mm. from the bottom, the color standards are prepared according to method of Muer and Hale.[9] These standards are prepared as follows:

(a) *Copper sulfate solution:* Dissolve 1.5 g. of copper sulfate ($CuSO_4 \cdot 5H_2O$) and 1 ml. of concentrated sulfuric acid in distilled water and dilute to 100 ml.

(b) *Potassium dichromate solution:* Dissolve 0.25 g. of potassium dichromate and 1 ml. of concentrated sulfuric acid in distilled water and dilute to 100 ml.

The quantities of these solutions used are given in Table 53:

TABLE 53.—STANDARDS FOR DETERMINATION OF CHLORINE WITH *o*-TOLIDINE

Chlorine p.p.m.	Potassium Dichromate Solution ml.	Copper Sulfate Solution ml.
0.01	0.18	0.3
0.02	0.32	0.5
0.04	0.61	1.0
0.06	0.87	1.4
0.08	1.1	1.7
0.10	1.3	1.9
0.15	1.7	1.9
0.20	2.1	2.0
0.25	2.6	2.0
0.30	3.0	2.0
0.35	3.4	2.0
0.40	3.8	2.0
0.50	4.7	2.0
0.60	5.5	2.0
0.70	6.4	2.0
0.80	7.2	2.0
0.90	8.1	2.0
1.00	9.0	2.0

After mixing the quantities of copper sulfate and potassium dichromate solutions indicated in the above table, the mixtures are diluted with distilled water to 100 ml.

For an accuracy of 0.1 p.p.m. of chlorine, the copper sulfate solution and the potassium dichromate solution should each be diluted to 0.1 strength with distilled water, and ten times the quantity indicated in the table used.

Procedure. Warm the water to be analyzed to 20-40° C. and place 100 ml. of the sample in a 300 mm.-100 ml. Nessler tube. Add 1 ml. of the *o*-tolidine reagent and allow to stand in a dark place until the color has developed. This usually requires from 5-15 minutes. In some cases color development occurs almost immediately and the color begins to fade in less than 5 minutes. When this occurs the reading should be made promptly after the development of the maximum color. Compare with a series of color standards.

If the solution contains more than 1.0 p.p.m. of chlorine, add 5 ml. of the reagent and compare in 15 minutes with standards prepared according to Table 54:

TABLE 54.—STANDARDS FOR DETERMINATION OF CHLORINE WITH *o*-TOLIDINE

Chlorine p.p.m.	Potassium Dichromate Solution ml.	Copper Sulfate Solution ml.
1.0	9	8
2.0	16	8
3.0	22	8
4.0	28	8
5.0	33	8
6.0	38	8
7.0	44	8
8.0	50	8
9.0	57	8
10.0	66	8

After mixing the quantities of copper sulfate and potassium dichromate indicated in the above table, dilute with distilled water to 100 ml. The copper sulfate and potassium dichromate solutions are prepared as described above.

Interference by nitrites in concentrations lower than 0.3 p.p.m. is largely avoided by making the color comparison within 15 minutes of the time of addition of the reagent, and keeping the tube in absolute darkness during this period. If these precautions are not carefully followed, nitrites may cause a yellow color, probably due to a partial hydrolysis of the diazonium salt.[14]

If the water has been treated with ammonia, the presence of chloramines may retard color development, but by warming to at least 20° C., this is largely eliminated.

At a pH of less than 4.0, the color due to chlorine varies from a pale yellow at a very low concentration, to an orange at a high concentration. If a green color develops, as may be the case with natural alkaline waters, or waters which have been treated with lime, the above procedure cannot be used.

If the quantities of iron, manganese and nitrite exceed those permissible in the above method, carry out the chlorine determination by one of the following modifications of the above procedure:

Reagents. *o-Tolidine solution:* Prepare as described above.

Hydrochloric acid solution: Dilute 300 ml. of concentrated hydrochloric acid with 700 ml. of distilled water.

Magnesium sulfate solution: Dissolve 20 g. of magnesium sulfate in 100 ml. of distilled water.

Sodium hydroxide solution: Dissolve 19 g. of sodium hydroxide in 100 ml. of distilled water. Titrate and adjust to 4.5 N. Some sodium hydroxide may have an appreciable chlorine demand. This should be determined as follows:

Place 10 ml. of the 4.5 N sodium hydroxide solution in a 100-ml. Nessler tube and add 0.2 ml. of a 100 p.p.m. standardized chlorine solution prepared from calcium hypochlorite. Allow to stand 30 minutes and add 90 ml. of zero-demand distilled water, 10 ml. of 4.5 N hydrochloric acid and 1 ml. of *o*-tolidine reagent and 2 ml. of dilute hydrochloric acid reagent. If residual chlorine is indicated, the sodium hydroxide may be regarded as having no chlorine demand. If more than 0.2 ml. of 100 p.p.m. chlorine solution is required, add a volume sufficient to produce a slight residual in the stock solution of 4.5 N sodium hydroxide, and allow the mixture to stand overnight so that the slight excess of chlorine may be absorbed before using.

If the regular procedure described above gives unsatisfactory results due to interference by nitrite, or because the iron content is above 0.3 p.p.m., and less than 1.0 p.p.m., use the following procedure:[15]

Procedure. To 100 ml. of the water to be analyzed in a Nessler tube, add 1 ml. of *o*-tolidine reagent and 1 ml. of the hydrochloric acid reagent. Mix thoroughly, place the tube in the dark for at least 5 and not more than 15 minutes, and then read immediately after the color is fully developed.

This procedure may also serve to eliminate the blue or green color which often appears when the pH of the sample is too high. If the quantity of manganic manganese exceeds 0.01 p.p.m., or if ferric iron is present in quantities greater than 1.0 p.p.m. use the following procedure: [15]

Procedure. To 200 ml. of the sample, add 2 ml. of magnesium sulfate solution and 2 ml. of 4.5 N sodium hydroxide solution. Mix thoroughly, distribute in tubes, and centrifuge at least at 1000 r.p.m. for 3 minutes. Decant off the supernatant liquid into a 300 mm.-100 ml. Nessler tube. Warm to at least 20° C. as in the regular procedure, add 2 ml. of hydrochloric acid reagent and 1 ml. of *o*-tolidine reagent. Mix, place the tube in the dark, and allow the color to develop for at least 5 and not more than 15 minutes. Compare with color standards.

o-Tolidine may also be used to determine chlorine in air.[16,17] Porter [16] recommends the following procedure:

Procedure. Place 10 ml. of *o*-tolidine reagent (page 464) in a test tube. Close the tube with a two hole rubber stopper which is provided with a long entrance tube and a capillary which extends beneath the surface of the liquid, and a short outlet tube. Connect the outlet tube to another tube which enters a large bottle. This bottle is fitted with a two hole rubber stopper containing as a second tube a long exit tube extending nearly to the bottom of the bottle. Fill the bottle with water to serve as a syphon and also to measure the volume of water removed in order to estimate the volume of air drawn through the *o*-tolidine solution. Aspirate 50-500 ml. of air through the reagent solution at a moderate speed. Rinse into a Nessler tube, dilute to 100 ml. and after 5 minutes compare with suitable color standards.

The use of *o*-tolidine as a reagent for chlorine in water, sewage and other materials has been extensively studied by many investigators.[18-34]

Detection and determination of iodide and iodate. *o*-Tolidine reacts with iodine in a neutral solution to give a bluish-green color similar to that with chlorine. Lange and Ward[85] have used this reaction for the determination of small quantities of iodides and iodates, after converting by oxidation and reduction respectively to free iodine. The reaction is sensitive to 0.01 mg. of iodine in 15 ml. of water.

Reagents. *o-Tolidine solution:* Dissolve 1 g. of *o*-tolidine in 150 ml. of 95 per cent alcohol.

Standard iodide solution: Dissolve 0.0131 g. of potassium iodide in water and dilute to 1 liter. One ml. of this solution contains 0.01 mg. of iodine.

Procedure. To 25 ml. of solution containing 0.01-0.1 mg. of iodide, add sufficient 1 per cent sodium hydroxide solution to make the mixture alkaline. Add 10 ml. of 3 per cent hydrogen peroxide to oxidize nitrites and evaporate the mixture to 20 ml. Filter, and wash with hot water and then add sulfuric acid until neutral to litmus. Evaporate the mixture to a little less than 30 ml. and divide into two equal parts.

To one part add 0.5 ml. of the *o*-tolidine reagent and dilute to 15 ml. Saturate the second portion with hydrogen sulfide, and then completely remove the excess hydrogen sulfide by boiling. Cool, and add 0.5 ml. of the *o*-tolidine solution. Dilute to 15 ml. and mix by shaking.

Prepare a series of standards containing from 1 to 10 ml. of standard iodide solution and to each add 0.5 ml. of *o*-tolidine reagent. Dilute to 15 ml. To the two unknown solutions and the standards add 5 ml. of 3 per cent hydrogen peroxide as rapidly as possible and shake well. Let stand for 5 minutes and compare. The blue color changes to a brown and a precipitate may form after 10 minutes.

The unknown solution which is treated with hydrogen sulfide gives the total quantity for both iodide and iodate. The other solution gives the value for iodide only. The amount of iodate may be determined by difference.

Detection and determination of gold. A reagent prepared by dissolving 1 g. of *o*-tolidine in a liter of 10 per cent hydrochloric acid gives a delicate test for chloroauric acid.[86-88] A solution containing 1 part of gold in 1,000,000 parts of water gives a bright yellow color with 1 ml. of this reagent. About three minutes are required for the color to develop fully and it is then permanent for about thirty minutes. With 1 part of gold in 20,000,000 parts of water, the yellow color can just be detected in a depth of 100 mm. of liquid.

Procedure. Make 25 ml. of the solution to be tested slightly acid with hydrochloric acid and add 1 ml. of a solution of 0.1 g. of *o*-tolidine in 100 ml. of 1:10 hydrochloric acid. Mix well and compare after 3 minutes with a standard similarly and simultaneously prepared.

Large quantities of strong mineral acid should not be present. The following metallic chlorides in dilute hydrochloric acid give no color reaction with *o*-tolidine: Aluminum, antimonic, barium, bismuth, cadmium, calcium, chromium, cobalt, copper, iridium, lead, magnesium, mercury, manganous, nickel, platinum, potassium, rhodium, sodium, strontium, stannic, uranium and zinc.

Ruthenium and ferric salts give a yellow color. Vanadates which have been acidified with dilute hydrochloric acid give a color reaction, while molybdates similarly acidified do not. Osmium tetroxide gives a yellow color, but this changes to green on standing. Sodium tungstate acidified with hydrochloric acid gives a precipitate, but no yellow color. Free chlorine or nitrous acid must be absent, since these substances give color reactions with *o*-tolidine. A green color is obtained if considerable copper is present, but a color comparison may be made in the presence of copper by tinting the standard gold solution to a similar extent with a copper salt.

Detection and determination of manganese. Manganic compounds react with *o*-tolidine to yield the same yellow color as obtained in the determination of chlorine.[20,39] This color is not produced with manganous salts, so a mild preliminary oxidation in an alkaline solution is necessary in carrying out the determination.

Procedure. To 100 ml. of water in a flask add 5-6 drops of 1 per cent sodium hydroxide solution until the mixture is alkaline to phenolphthalein. Bubble oxygen through the solution for 10 minutes or clean air for 30 minutes to oxidize manganous to the manganic state. If more than 0.5 p.p.m. of iron is present, add 5 ml. of 85 per cent phosphoric acid.

Transfer the solution to a Nessler tube and add 5 ml. of *o*-tolidine reagent prepared as described under the determination of chlorine. Allow to stand 15-20 minutes and compare with permanent standards as described in the determination of chlorine. To obtain the manganese equivalent of the chlorine standards, multiply the results in terms of chlorine by 1.25.

Detection of iron, vanadium, cerium and chromium. Manganese, iron, chromium, vanadium and cerium may be detected with *o*-tolidine by reactions which are similar to those employed with benzidine.[20] These reactions are probably due to formation of similar quinoid oxidation products. One part of ceric ammonium sulfate in 10,000 parts of solution gives a blue color with *o*-tolidine, whereas no color is obtained with lanthanum, thorium, zirconium, yttrium and neodymium and praseodymium. The cerium test must be carried out in the absence of manganese, iron, chromium and other ions which give similar reactions.

In making the chromate test, a mixture of *o*-tolidine and hydrogen peroxide may be used instead of pure *o*-tolidine. In this way the sensitivity of the reaction is markedly increased, probably due to the formation of a perchromate, which has a greater oxidation potential than the dichromate. In making this test, a mixture of equal parts of 1 per cent *o*-tolidine solution and 30 per cent hydrogen peroxide gives good results. This test is about seventy times as sensitive as that with benzidine.[40,41]

Detection and determination of silver. *o*-Tolidine reacts like benzidine with silver ions to give a blue color reaction which may be used for the detection of silver. With benzidine this reaction has been given as follows:

$$2Ag^+ + O_2 + 4H^+ + 2NO_3^- + 2Bzd \rightarrow 2Ag + 2H_2O + Bzd\ Blue \cdot 2HNO_3$$

o-Tolidine, however, appears to give with silver a more intense color reaction and at a greater rate. To detect silver, proceed as follows:[42]

Procedure. Add 2-3 drops of concentrated nitric acid to 0.1-0.5 ml. of solution to be tested and evaporate to dryness. Ignite gently and add a few drops of water. Place 1 drop of a 1 per cent alcoholic solution of *o*-tolidine on a strip of filter paper, and add 1 drop of the prepared solution with a capillary pipet to the center of the moist spot. Wet the spot with an acetate buffer of pH 4.0. A blue color appears if silver is present. This reaction is sensitive to 0.03γ of silver at a dilution of 1:100,000.

Kul'berg and Serebryanii[43] have used this reaction for the colorimetric determination of silver:

Procedure. Place 1-2 ml. of the solution to be analyzed in a 10-15 ml. Erlenmeyer flask and add 1 ml. of an acetate buffer of pH 4 and 0.25 ml. of a 1.0 per cent alcoholic solution of *o*-tolidine. Allow the mixture to stand for 15 minutes to develop the blue color and then transfer to a colorimeter and compare with standards containing known quantities of silver. The reaction and comparison should be carried out in solutions at a temperature of 0-15° C. At temperatures above 20° C. the solutions decompose.

The smallest quantity of silver determinable by this method is 0.015 mg. in 1-2 ml., and the minimum amount satisfactorily determined is 7.5 mg. per liter. The average error of this method is about 3 per cent for quantities of silver of 0.04 mg. or greater. For smaller quantities the error may be as great as 10-15 per cent.

Detection and determination of cobalt. Brau[44] has suggested the use of *o*-tolidine in place of Benzidine in Chiarottino's[45] well-known reaction for cobalt, which depends upon the orange-red coloration that is formed when a solution of cobalt salt is treated with an alcoholic solution of benzidine and dimethylglyoxime. Spacu and Macrovici[46] recommend the following procedure:

Procedure. To the solution to be tested add 5 ml. of a 1 per cent alcoholic solution of dimethylglyoxime and shake. Then add 2 ml. of a 1 per cent alcoholic solution of *o*-tolidine and again shake. A red color appears with as little as 0.0002 mg. of cobalt per ml. The limiting concentration of this test is 1:500,000.

Small quantities of cobalt may be determined by comparing the red color obtained in the above reaction with that formed with standard cobalt solutions. As little as 0.001 mg. of cobalt per ml. can be determined with an error of about 0.5 per cent.

Detection and determination of lead. *o*-Tolidine may be used to replace benzidine in the test for lead, which depends upon the conversion of lead to lead peroxide and the subsequent oxidation of *o*-tolidine to the blue compound.

Bolotov [47] has used this reaction for the determination of small quantities of lead.

Procedure. Electrolyze 50 ml. of the solution to be analyzed in the presence of nitric acid and 2 drops of 25 per cent sulfuric acid, using a copper cathode and a platinum anode. Wash the lead peroxide which is deposited on the anode into 3 ml. of a solution prepared by dissolving 0.1 g. of *o*-tolidine in 10 ml. of concentrated hydrochloric acid and 90 ml. of water. Dilute this solution with water and compare the resulting color with that of a standard prepared by treating 1 ml. of 0.0001 N potassium permanganate with the *o*-tolidine solution. This standard gives a color comparable to that of 0.014 mg. of lead.

From 5 to 20γ of lead has been determined by this method with an average error of 4 per cent and a maximum error of 6 per cent. With 2γ of lead the error ranges from -5 to $+10$ per cent, and for 50γ of lead the average error is -12 per cent.

Detection of thallium. *o*-Tolidine may be used in place of benzidine for the detection of thallic thallium. This reaction is based on the oxidation of *o*-tolidine to the blue compound by thallic hydroxide. This reaction is recommended by Wenger and co-workers.[69]

Detection of osmium. Kul'berg [48] has used *o*-tolidine in a reaction to detect osmium. This test is based upon the direct oxidation of *o*-tolidine with osmium tetroxide, or the activation of chlorate by the action of osmium tetroxide.

Detection and determination of copper. *o*-Tolidine is used like benzidine to precipitate copper in the presence of ammonium or potassium thiocyanate. This reaction has been used by Spacu [49] for the detection of copper and thiocyanates. When a very dilute solution of a cupric salt is treated with a few drops of thiocyanate, and not more than 2 drops of a 2 per cent freshly prepared solution of *o*-tolidine in alcohol, a very characteristic, blue, flocculent precipitate of $[CuTld](SCN)_2$ is formed. In this formula Tld represents 1 molecule of *o*-tolidine.

Folcini[50] has used a similar procedure for copper and thiocyanate in which various polysulfides and amines have been substituted for the thiocyanates and benzidine or *o*-tolidine.

The precipitation of copper with ammonium thiocyanate and *o*-tolidine from a nearly neutral aqueous solution is quantitative.[51,66] The ammonium thiocyanate is added in a 4- or 5-fold excess, although the alcoholic solution of *o*-tolidine should be present only in very slight excess. The copper *o*-tolidine complex is somewhat soluble in an aqueous alcoholic solution. The copper compound may be ignited to copper oxide, which may be weighed for the determination of copper.

When a solution of *o*-tolidine and thiocyanate is mixed with a cupric salt, the *o*-tolidine is oxidized to a meriquinoid compound similar to benzidine blue. This reaction depends upon the increase in the oxidation potential of the cupric salt, due to the formation of insoluble cuprous thiocyanate. This reaction is, represented by the following equation:

$$2Cu^{+2} + 2Tld + 2SCN^- \rightarrow 2CuCNS + Tld\ Blue$$

Since *o*-tolidine is more readily oxidizable, and gives a more stable color than benzidine, the *o*-tolidine test is somewhat more sensitive than that with benzidine. This reaction has been used by Kul'berg[52,54] for the detection of small quantities of copper. The test is carried out as follows:

Reagent. Dissolve 0.1 g. of *o*-tolidine and 0.5 g. of ammonium thiocyanate in 5 ml. of acetone.

Procedure. Place a drop of the reagent on a strip of filter paper and add a drop of the neutral or slightly acid solution to be tested. A blue stain appears if copper is present, and the intensity of the color is proportional to the amount of copper present. As little as 0.003γ of copper can be detected at a dilution of 1:5,000,000.

Silver, mercurous, iron, trivalent thallium, ceric and gold salts and chloroplatinic acid interfere with this test. Silver salts are precipitated as the chloride, and the effect of iron salts is neutralized by the addition of an alkali fluoride. The remaining strongly oxidizing ions are rendered harmless by reduction with bismuth amalgam. Manganese salts may interfere when present in large quantities.

Thanheiser[55] has used this reaction for detecting copper in steel without destroying the sample. The surface of the steel is cleaned with emery and then treated with 1-2 drops of mineral acid. The drop is transferred to filter paper or a spot plate and tested as described above.

Gulyaeva and Itkina[67] have applied the *o*-tolidine reaction to the colorimetric determination of copper in rocks.

Detection of the platinum metals. Whitmore and Schneider[56] have studied the use of *o*-tolidine hydrochloride as a reagent for the microchemical detection of the platinum metals. The results obtained by adding a 5 per cent solution of *o*-tolidine hydrochloride to 2 per cent solutions of platinum metal salts is given in Table 55, which is taken from the work of Whitmore and Schneider.

TABLE 55.—REACTION OF *o*-TOLIDINE WITH THE PLATINUM METALS

Test Material	Description
$RuCl_3$	Some small, brownish-purple clusters of very small, needle-shaped crystals develop around the edge of the drop.
$RhCl_3$	As the drop evaporates a few, very pale brown, slender crystals appear at the edge of the drop.
$PdCl_2$	A very dense, orange colored precipitate forms immediately. This is composed of an entangled mass of a great many very small, needle-shaped crystals.
Na_2OsCl_6	A great many, long, bright-yellow, needle-shaped, crystals form immediately. These occur singly, also in clusters, forming an entangled mass throughout the drop.
$IrCl_4$	A very dense, purple precipitate forms immediately. This is composed of a great many, tiny, needle-shaped crystals forming an entangled mass over the entire drop.
H_2PtCl_6	A very dense, pale-yellow, precipitate forms immediately. This precipitate consists of an entangled mass of a great many long slender, needle-shaped crystals.
$AuCl_3$	A very dense, bright-purple amorphous precipitate forms immediately. At the edge of this precipitate a few, very small irregular, branching forms appear.

Detection and determination of mercury. A solution of *o*-tolidine in 50 per cent acetic acid reacts with solutions of the mercury halides to form insoluble complexes of the form $[HgTld]Br_2$.[57] These salts are sufficiently characteristic and insoluble to be used for the determination of mercury.

Determination of tungsten. Tungstic acid is quantitatively precipitated with *o*-tolidine hydrochloride while *o*-tolidine phosphate is soluble. Knorre[58] has used this reaction for the separation of tungstic acid from phosphoric acid. *o*-Tolidine is preferred to benzidine, since *o*-tolidine phosphate is more readily soluble than the corresponding benzidine compound. The following procedure is used for the separation:

Reagent. Suspend 20 g. of *o*-tolidine in water and add 28 ml. of concentrated hydrochloric acid and warm. Filter and dilute to 1 liter. Ten ml. of this solution precipitates 0.22 g. of WO_3.

Procedure. Heat 300-400 ml. of dilute solution to be analyzed, add 3 ml. of hydrochloric acid and heat to boiling. Precipitate tungsten while hot by adding an excess of *o*-tolidine hydrochloride solution. Cool completely, filter, and wash the precipitate with the dilute *o*-tolidine solution and ash in a platinum crucible. Decompose the residue by heating with sodium carbonate, dissolve in water, and repeat the precipitation to remove all phosphate.

Detection of hydrogen peroxide. In the presence of ferrous iron, *o*-tolidine reacts with hydrogen peroxide to give a blue color. This reaction has been used by Kul'berg and Matveev [59] for the detection of small quantities of hydrogen peroxide:

Procedure. Place 1 drop of a 1 per cent alcoholic solution of *o*-tolidine on a strip of filter paper, and add 1 drop of an acetate buffer of pH 4. Next add a drop of a 1 per cent ferrous sulfate solution and finally a drop of the solution to be tested. In the presence of hydrogen peroxide a blue color appears. As little as 0.025γ of hydrogen peroxide at a concentration of 1:24,000 can be detected.

Determination of sulfate. Like benzidine, *o*-tolidine forms an insoluble precipitate with sulfates. This reaction may be used to determine sulfates, but offers no advantages over the older and better-known methods.[60]

Detection of hydrogen cyanide. *o*-Tolidine is used in a test for cyanides which is based upon the oxidizing action produced when a cupric salt is added to hydrogen cyanide. The following test is recommended by Moir [61] for the detection of hydrogen cyanide in air:

Procedure. Moisten a strip of filter paper with a reagent prepared by dissolving 1 g. of *o*-tolidine, 1.5 g. of copper acetate and 0.5 g. of glacial acetic acid in 100 ml. of water. A blue color appears when this paper is exposed to gas containing as little as 1 part of hydrogen cyanide in 2,000,000 parts of gas.

Detection and determination of nitrate. Nitrates may be determined indirectly by a method developed by Phelps and Shoub.[62] In the presence of a chloride, the solution containing a nitrate is evaporated to dryness. *o*-Tolidine is then added in a hydrochloric acid solution and the mixture is treated with concentrated sulfuric acid. Free chlorine, which is liberated by the action of the nitrate, then reacts with *o*-tolidine to give the characteristic blue color.

According to the authors this method appears to eliminate most of the objectionable features of other methods.

Reagents. *o-Tolidine solution:* Dissolve 0.4 g. of *o*-tolidine in 100 ml. of N hydrochloric acid.

Sodium hydroxide-sodium chloride solution: Dissolve 5 g. of sodium hydroxide and 1.5 g. of sodium chloride in water and dilute to 100 ml.

Standard nitrate solution: Dissolve 0.72 g. of pure potassium nitrate in water and dilute to 1 liter. Then dilute 10 ml. of this solution to 100 ml. One ml. of the latter solution is equivalent to 0.01 mg. of nitrogen as nitrate.

Procedure. Place 25 ml. of the solution to be analyzed in a 50-ml. Erlenmeyer flask and add 0.5 ml. of the sodium hydroxide-sodium chloride solution. Boil for 30 seconds, cool, and dilute to a definite volume. Transfer 1 ml. of the supernatant liquid to a 3-inch evaporating dish and evaporate to dryness on a water-bath. With samples containing more than 10 p.p.m. of nitrate, use a proportionately smaller quantity of the supernatant liquid and with less than 1 p.p.m. use 10 ml. of the liquid.

Now add 0.2 ml. of the *o*-tolidine solution and mix well with the residue. Be careful and add no more than 0.2 ml. of the reagent. Next add 0.5 ml. of concentrated sulfuric acid, which is allowed to flow slowly down the sides of the dish. Do not mix. Allow the mixture to stand for 5 minutes, and then tilt the dish so as to wet the sides with the liquid. Allow to stand for 30 seconds and dilute with 5 ml. of water. Pour the mixture into a comparison tube and dilute to 10 ml. Compare with standards within 5 minutes.

o-Tolidine hydrochloride yields a white crystalline compound with nitrate which may be used for the microchemical detection of this ion.[68]

Detection and determination of nitrite. *o*-Tolidine reacts with nitrite in a dilute acetic acid solution to form an orange-red color. Primot[63] used this reaction for the detection and determination of nitrites in water:

Procedure. Add 5 drops of a 1-1.5 per cent solution of *o*-tolidine in 30-40 per cent alcohol and 5 drops of acetic acid to 10 ml. of the water to be analyzed. An orange-red color is obtained with as little as 0.01 g. of nitrous acid per liter.

Sulfates and free mineral acids must be removed before applying this test.

By comparing the orange-red color with that of standard solutions containing known quantities of nitrite, small quantities of nitrites may be determined. The maximum intensity of the color reaction is attained in about 30 minutes.

Detection of sulfur chlorides. A solution of 0.01 M S_2Cl_2 in pure carbon tetrachloride reacts with five times as much 0.01 M *o*-tolidine in a mixture of equal volumes of carbon tetrachloride and ethyl alcohol to form an intense red color which is fairly stable in the dark. An excess of the *o*-tolidine solution is necessary to prevent precipitation. Neither $SOCl_2$ nor SO_2Cl_2 gives any color with *o*-tolidine. SCl_2 gives a color with the reagent but it is much less intense than that with S_2Cl_2.[65]

Determination of oxygen. A colorimetric method based upon the reaction of *o*-tolidine with copper can be used to determine oxygen in water if the oxygen content ranges from 0.01-1.0 mg. per liter.[65] When ammonium hydroxide is added to water containing a little solid cuprous chloride, the latter dissolves due to the formation of colorless, soluble cuprous ammonium chloride. If dissolved oxygen is present, the cuprous salt is immediately oxidized to the cupric state. The determination of the cupric ions so formed serves for the indirect determination of oxygen. In a method described by Zanko,[65] a part of the ammoniacal copper solution is evaporated until ammonium chloride begins to crystallize, the solution is cooled, the crystals dissolved, 1-2 ml. of 0.3 per cent gelatin solution and 0.5-1.0 ml. of 1.0 per cent *o*-tolidine solution added. The solution is then diluted with a saturated solution of ammonium chloride and the copper determined colorimetrically.

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o-TOLUIDINE

Synonym: 2-Methylaniline, 2-aminotoluene

C_7H_9N Mol. Wt. 107.15 Beil. Ref. XII, 772.

$$CH_3—C_6H_4—NH_2$$

Use: Detection of gold, hydrogen cyanide, hydrogen peroxide, iridium, nickel, osmium, palladium and platinum.

Determination of cerium, lanthanum, neodymium, praseodymium, thorium and zirconium.

o-Toluidine is a light yellow liquid, which gradually becomes reddish-brown upon exposure to light and air. It boils at 199° C., and has a density of 1.008. It is only slightly soluble in water, but is soluble in alcohol, ether and dilute acids.

Preparation: Mix 500 g. of *o*-nitrotoluene and 80 ml. of water and heat to boiling, and add 16 g. of hydrochloric acid. Then add slowly to the hot solution 500 g. of powdered iron and boil for one-half hour under reflux. Steam distill and separate the amine from the distillate. If the nitro compound contains both the ortho and para isomers, the oil obtained in the steam distillation consists of a mixture of *o*- and *p*-toluidine. These may be separated as follows:

(a) Separate the oil from the water and add ice and salt and stir. The hydrate of *p*-toluidine separates as a whitish-yellow crystalline compound. Filter through an ice filter and carefully press out the crystals to remove any adhering *o*-toluidine. Separate the *o*-toluidine from the filtrate by pouring into a separatory funnel and allowing to stand until two layers separate. The addition of salt aids in the separation. Dry the amine over solid sodium hydroxide and distill. Recrystallize the para compound from alcohol.[1]

(b) Pure *o*-toluidine is prepared as follows: Dissolve the mixture containing the ortho and para isomers in hydrochloric acid until the mixture is slightly acid to Congo red, and then add water until the mixture is saturated at ordinary temperature. Now add a saturated aqueous solution of sodium ferrocyanide with shaking to precipitate *o*-toluidine hydroferrocyanide. Filter, wash the precipitate with a little water, and then with very dilute hydrochloric acid. Dry, and decompose the salt with sodium hydroxide. Extract with ether, and dry the ether solution with potassium carbonate. Remove the ether by evaporation and distill. *o*-Toluidine distills at 198° C.[2]

Detection of nickel. Crystals, claimed by Martini[3] to be $[C_6H_4CH_3NH_2 \cdot HSCN]_4[Ni(NH_3)_4](SCN)_2$, are obtained by treating 1 drop of a 1 per cent nickel chloride solution with 1 drop of a concentrated solution of ammonium thiocyanate and 1 drop of *o*-toluidine. These crystals may be identified under a polarization microscope. Langer[4] claims that the reaction between nickel and *o*-toluidine does not yield the theoretical complex of Martini, but rather forms a compound having the formula, $[Ni(NH_3)_2(C_6H_4CH_3NH_2)_2](SCN)_2(H_2O)_2$.

Detection of platinum metals. Whitmore and Schneider[5] have studied the use of *o*-toluidine hydrochloride as a microchemical reagent for the detection of platinum metals. The results obtained by adding a solid fragment of the hydrochloride to a 1 per cent solution of the platinum salts is given in Table 56, which is taken directly from the work of Whitmore and Schneider:

TABLE 56.—REACTION OF PLATINUM METALS

Test Material	Description
$RuCl_3$	No apparent reaction.
$RhCl_3$	No apparent reaction.
$PdCl_2$	A dense, yellow, amorphous precipitate forms.
Na_2OsCl_6	A very scant, amorphous precipitate forms around the reagent particle, then on standing a short time extremely long, needle-shaped crystals develop at the circumference of the drop. These grow to great length reaching the center of the drop.
$IrCl_4$	A green, flocculent, precipitate forms immediately.
H_2PtCl_6	Very long, yellow, needle-shaped crystals develop around the circumference of the drop. These grow to an enormous length toward the center of the drop.
$AuCl_3$	A green, amorphous, precipitate is formed immediately.

Determination of the rare earths. *o*-Toluidine may be used as a precipitant for zirconium, thorium, cerium, lanthanum, neodymium, and praseodymium.[6]

Detection of hydrogen cyanide. Kozlovskii and Penner[7] have studied the effect of the use of different amines upon the reaction between hydrogen cyanide and alloxan. They have found that *o*-toluidine is about the least sensitive of the amines employed.

Detection of hydrogen peroxide. Various amines when mixed with potassium dichromate and hydrogen peroxide give a yellow color in the presence of oxalic acid. This reaction has been used by Ilosvay and Ilosva[8] for the detection of hydrogen peroxide.

Reagent. Add five drops of *o*-toluidine to 0.03 g. of potassium dichromate dissolved in a liter of water.

Procedure. Mix 5 ml. of the solution to be tested with 5 ml. of the reagent and 1 drop of a 5 per cent solution of oxalic acid. The test is sensitive to about 1 part in 1,000,000, although about six hours are required for the development of the yellowish-green color at this dilution.

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4. A. Langer, *Chem. Listy.* **32**, 66-9 (1938) ; *C.A.* **32**, 5333 (1938).
5. W. F. Whitmore and H. Schneider, *Mikrochemie.* **17**, 279-319 (1935).
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m-TOLUIDINE

Synonym: 3-Aminotoluene, 3-methylaniline

C_7H_9N Mol. Wt. 107.15 Beil. Ref. XII, 853.

$CH_3—C_6H_4—NH_2$

Use: Detection of nitrite, osmium, palladium, platinum and ruthenium.

m-Toluidine is a colorless liquid. It has a sp. gr. of 0.990. And boils at 203-204° C. It is slightly soluble in water, but is soluble in alcohol, ether and dilute acids.

Preparation: *m*-Toluidine is prepared by reducing *m*-nitrotoluene with tin and hydrochloric acid or with stannous chloride and hydrochloric acid. The compound is recovered by distilling with steam and extracting the distillate with ether. The ether is removed by distillation and the *m*-toluidine recovered by distilling at 203-204° C.[1]

Detection of nitrite. When a little *m*-toluidine in 1:1 acetic acid is added to a neutral solution containing a nitrite, a red or orange-red color forms, which is both intense and persistent.[2] The colored compound is extractable with ether. Ferric iron and other oxidizing agents give similar reactions, but with the latter compounds the color is not soluble in ether. The test fails in the presence of chromic acid and the halogens.

Reactions of the platinum metals. Whitmore and Schneider[3] have used *m*-toluidine hydrochloride as a microchemical reagent for metals of the platinum group. The results obtained by adding a solid fragment of the hydrochloride to a 1 per cent solution of platinum metal salts is given in Table 57, which is taken from the work of Whitmore and Schneider.

TABLE 57.—REACTIONS OF PLATINUM METALS WITH *m*-TOLUIDINE

Test Material	Description
$RuCl_3$	A very faint greenish, flocculent precipitate appears on standing.
$RhCl_3$	No apparent reaction.
$PdCl_2$	A yellow, amorphous precipitate is formed. On standing, a few very small radiating clusters of prisms form at the circumference.
Na_2OsCl_6	On standing, some long, slender, bright-yellow, needle-shaped crystals develop at the circumference.
$IrCl_4$	A scant green flocculent precipitate is formed.
H_2PtCl_6	A great mass of hair-like sheaves, made up of very long, slender crystals develop around the circumference and extend inward toward the center. Similar tufts also develop throughout the drop. A few hexagonal prisms with broken ends are also formed.
$AuCl_3$	A green amorphous precipitate is formed.

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3. W. F. Whitmore and H. Schneider, *Mikrochemie.* 17, 279-319 (1935).

p-TOLUIDINE

Synonym: 4-Aminotoluene

C_7H_9N Mol. Wt. 107.15 Beil. Ref. XII, 880.

$$CH_3—C_6H_4—NH_2$$

Use: Detection of gold, iridium, nitrate, osmium and platinum.

p-Toluidine consists of white lustrous plates which melt at 44-45° C. and boil at 200-201° C. It is soluble in about 135 parts of water, but dissolves readily in alcohol, ether, methyl alcohol, acetone and carbon disulfide.

Preparation: *p*-Toluidine is prepared by the reduction of *p*-nitrotoluene with iron and hydrochloric acid.[1,2] For details, see section on *o*-toluidine.

Detection of nitrate: Longi[3] has used *p*-toluidine for the detection of nitrate by a modification of Braun's test.[4,5]

Procedure. Add several drops of a solution of *p*-toluidine in dilute sulfuric acid to the solution to be tested, and carefully add the mixture to a tube containing concentrated sulfuric acid so as to form two layers. A mixture of *p*-toluidine and aniline is said to be more sensitive. One part of potassium nitrate in 32,000 parts of water can be detected by the red ring which forms.

Chlorate, bromate, iodate, chromate and permanganate give an intense blue color. Nitrite yields a yellowish-color.

Detection of the platinum metals. Whitmore and Schneider[6] have investigated in the use of a 10 per cent *p*-toluidine hydrochloride solution as a microchemical reagent for the platinum metals. Results obtained are given in Table 58, which is taken directly from the work of Whitmore and Schneider:[6]

TABLE 58.—DETECTION OF THE PLATINUM METALS WITH *p*-TOLUIDINE HYDROCHLORIDE

Test Material	Description
$RuCl_3$	No apparent reaction.
$RhCl_3$	No apparent reaction.
$PdCl_2$	A very fine and dense yellow amorphous precipitate is formed.
Na_2OsCl_6	Irregular, bright-yellow forms and extremely long, needle-shaped crystals develop at the edge of the drop. Clusters of bright-yellow plates appear, also rectangular plates and small slender prisms.
$IrCl_4$	A bright red flocculent precipitate is formed immediately. Some very long, yellow, needle-shaped crystals develop at the circumference and grow toward the center of the drop.
H_2PtCl_6	There is an immediate formation of a dense mass of crystalline forms. These appear as radiating clusters of very thin plates.
$AuCl_3$	A very fine, red, granular precipitate forms.

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3. A. Longi, *Z. anal. Chem.* 23, 350 (1884).
4. C. D. Braun, *Z. anal. Chem.* 6, 71 (1877).
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6. W. F. Whitmore and H. Schneider, *Mikrochemie.* 17, 279-319 (1935).

1,2,4-TOLUYLENEDIAMINE Synonym: 1-Methyl-2,4-diaminobenzene

$C_7H_{10}N_2$ Mol. Wt. 122.17 Beil. Ref. XIII, 124.

$$CH_3—C_6H_3(NH_2)_2$$

Use: Detection of nitrite.

1,2,4-Toluylenediaminc is a crystalline solid melting at 99° C. It is readily soluble in alcohol, ether and boiling water.

Preparation. *2,4-Dinitrotoluene:* Heat 400 g. of toluene to 60° C. and during a period of 4 hours allow a mixture of 700 g. of concentrated sulfuric acid and 450 g. of nitric acid (44.1° Be.) to flow in. Shake for one-half hour and separate the resulting nitro compound from the acid. Then add during a period of 3 hours a mixture of 1350 g. of concentrated sulfuric acid and 450 g. of nitric acid (46.8° Be.), whereby the temperature is raised to 115° C.

Finally, warm the mixture with shaking for 1 hour on a boiling water-bath. Draw off the acid and pour the reaction product into boiling water.[1]

1,2,4-Toluylenediamine: 1,2,4-Toluylenediamine is prepared by the reduction of the dinitrotoluene with the aid of tin and hydrochloric acid.[2]

Detection of nitrites. A 3 per cent solution of 1,2,4-toluylenediamine in 5 per cent acetic acid when added to a neutral solution containing a nitrite gives a red or orange-red color which is intense and persistent. The coloring matter is soluble in ether. Ferric iron and other oxidizing agents give a similar color reaction but with these substances the color formed is not soluble in ether.[3]

1. A. Kayser, *Z. Farb.-u. Textilchemie.* 2, 32.
2. A. Ladenburg, *Ber.* 8, 1210 (1875).
3. A. Casolari, *Chim. Ind. Agr. Biol.* 14, 294 (1938); *C.A.* 33, 3292 (1939).

1,2,5-TOLUYLENEDIAMINE Synonym: 1-Methyl-2,5-diaminobenzene

$C_7H_{10}N_2$ Mol. Wt. 122.17 Beil. Ref. XIII, 144.

$$CH_3—C_6H_3(NH_2)_2$$

Use: Detection of vanadium.

1,2,5-Toluylenediamine is a crystalline solid melting at 64° C. and boiling at 273-274° C. It dissolves readily in water, alcohol, ether and hot benzene.

Preparation: 1,2,5-Toluylenediamine is prepared by the reduction of 2,5-dinitrotoluene [1] or 5-nitro-2-aminotoluene [2] with tin and hydrochloric acid.

Detection of vanadium. When a solution of 1,2,5-toluylenediamine in hydrochloric acid is added to a solution containng ammonium vanadate, a green and then a lilac color is obtained. This test is sensitive to 1 part of ammonium vanadate in 10,000 parts of solution.[3]

1. Br. Rozanski, *Ber.* 22, 2679 (1889).
2. F. Beilstein and A. Kuhlberg, *Ann.* 158, 352 (1871).
3. L. Rosenthaler, *Mikrochemie.* 23, 194-7 (1937); *C.A.* 32, 1609 (1938).

1,3,4-TOLUYLENEDIAMINE Synonym: 1-Methyl-3,4-diaminobenzene

$C_7H_{10}N_2$ Mol. Wt. 122.17 Beil. Ref. XIII, 148.

$$CH_3—C_6H_3(NH_2)_2$$

Use: Detection of hydrogen peroxide and nickel.

1,3,4-Toluylenediamine is a crystalline solid melting at 88.5° C. It is moderately soluble in cold water.

Preparation: 1,3,4-Toluylenediamine is obtained from 3-nitro-4-aminotoluene by reduction with tin and hydrochloric acid [1] or with sodium amalgam or zinc and alcoholic alkali.[2]

Detection of nickel. A bluish-purple precipitate of $Ni[C_6H_3CH_3(NH_2)_2]_2$ is formed by the action of 1,3,4-toluylenediamine on an ammoniacal solution of a nickel salt. This compound is partially soluble in pyridine, quinoline, piperidine and aniline, with the formation of a purple-colored solution.[3]

Detection of hydrogen peroxide. Hydrogen peroxide may be detected by the red color which is obtained in the reaction with 1,3,4-toluylene diamine and potassium dichromate:[4]

Reagent. Dissolve 0.05 g. of 1,3,4-toluylene diamine in 1 liter of water and add 0.015 g. of potassium dichromate.

Procedure. To 5 ml. of the solution to be tested, add an equal volume of the yellow reagent and acidify with 5 per cent oxalic acid. A red color is obtained if hydrogen peroxide is present in a concentration of 1 part in 1,000,000.

1. F. Beilstein and A. Kuhlberg, *Ann.* 158, 351 (1871).
2. H. Limpricht, *Ber.* 18. 1404 (1885).
3. F. Feigl and M. Furth, *Monatsh.* 48, 445-50 (1927); *C.A.* 22, 199 (1928).
4. L. Ilosvay, *Ber.* 28, 2029 (1895).

TRIETHANOLAMINE

Synonym: Tri(hydroxyethyl)amine

$C_6H_{15}O_3N$ Mol. Wt. 149.19 Beil. Ref. IV, 285.

$$(CH_2(OH)—CH_2)_3N$$

Use: Detection of aluminum, antimony, bismuth, boron, cadmium, cobalt, chromium, copper, gold, iodine, iron, lead, manganese, mercury, molybdate, nickel, phosphate, silver, tin, vanadium and zinc.

Determination of antimony, hydrogen cyanide and tin.

Triethanolamine is a colorless viscous hygroscopic liquid which darkens on exposure to air. It melts at 20-21.2° C. and boils at 277-279° C./150 mm. Its sp. gr. is 1.124. Triethanolamine is miscible with water and alcohol and is soluble in chloroform. It is slightly soluble in benzene and ether. It is a strong base and combines readily with acids to form salts.

The technical product is a mixture consisting of about 70-75 per cent triethanolamine with 20-25 per cent of diethanolamine and up to 5 per cent monoethanolamine.

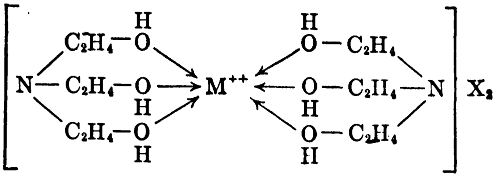
Reactions of triethanolamine with metals. Triethanolamine and solutions of metallic salts give reactions which may be used for the detection of a number of cations.[1-9] Jaffe[1] has studied the reactions obtained when a 20 per cent aqueous solution of triethanolamine is added to solutions of various metallic salts. The results are given in Table 59.

When pure anhydrous triethanolamine reacts with concentrated aqueous solutions of metallic salts, crystalline complex compounds composed of one mole of inorganic salt and two moles of organic base are formed. Thus, with nickel chloride, cadmium sulfate and calcium chloride the following compounds are

TABLE 59.—REACTIONS OF TRIETHANOLAMINE WITH CATIONS

Ion	Results	Remarks
Mercurous	Gray precipitate	Separation of mercury.
Lead	White precipitate	Insoluble in excess reagent.
Silver	Yellowish-brown precipitate	Soluble in excess reagent. Solution forms on standing, or more quickly by heating to boiling. By shaking with 4 per cent formaldehyde, a silver mirror with 0.01 per cent silver.
Copper	Blue solution	Similar to ammonia.
Cadmium	Powdered white precipitate	Soluble in excess reagent.
Mercuric	White precipitate	Gray on heating.
Bismuth	White precipitate	Insoluble in excess reagent.
Gold	A concentrated solution of gold salt yields a reddish-yellow precipitate which dissolves in an excess of reagent to form a yellow solution. Gold separates on heating as a black powder with a part being deposited as a gold mirror. With a large excess of the reagent (10-15 volumes) and careful heating, a blue-red solution is obtained, which quickly turns to a carmine red color with the simultaneous separation of a black deposit of gold. From dilute gold solutions, the color which appears on the addition of 2-3 drops of reagent and slight heating, is at first green and then blue with the simultaneous formation of a gold mirror. Very dilute solutions containing 0.000001 g. of gold per ml. form a red colloidial gold suspension.	
Tin	White precipitate	Insoluble in excess reagent.
Ferric	Amorphous red precipitate	Soluble in excess reagent.
Ferrous	Dirty green precipitate	Dark green with excess reagent.
Aluminum	Gelatinous white precipitate	Soluble in excess reagent.
Chromium	Blue gray precipitate	Partially soluble in excess reagent.
Manganese	A white precipitate which quickly changes to a dirty reddish-yellow. A brown color appears with sodium hydroxide which becomes stronger on shaking, and eventually changes to a dark green. On filtering, a brown precipitate is obtained and an emerald-green filtrate. If the original precipitate is directly dissolved in tartaric acid, a reddish-yellow solution is obtained. On the addition of an alkali a grass-green, and with excess alkali a dark yellow, and after strong dilution an emerald-green color forms. A reddish-brown precipitate separates with decolorization when this solution is allowed to stand in air. This reaction is characteristic for manganese.	
Zinc	White precipitate	Insoluble in excess reagent.
Nickel	Blue solution	In contrast to the reaction with ammonia, an intense emerald-green color appears on the addition of an alkali. This color may be used for the colorimetric determination of nickel.
Cobalt	Carmine-violet color	On the addition of tartaric acid, a reddish-white precipitate is formed, which is dissolved in excess reagent with carmine-red color. An intense violet color appears on the addition of an alkali. This reaction is characteristic for cobalt.

obtained: $NiCl_2 \cdot 2Tri$; $CdSO_4 \cdot 2Tri$; and $CaCl_2 \cdot 2Tri$, where Tri represents one molecule of triethanolamine. These compounds may have the following composition:



No precipitates are obtained directly with strontium or magnesium. chlorides.

Separation of cobalt and nickel. Raymond[10] used triethanolamine in a procedure for the separation of cobalt and nickel. The addition of an excess of triethanolamine to a mixture of cobalt and nickel salts does not permit a separation of the two metals, for the precipitation of nickel is always incomplete. In a strongly alkaline medium, however, and on heating, the nickel complex is completely decomposed while the cobalt compound remains in solution. Nickel hydroxide is precipitated quantitatively in an easily filterable form, although it passes into the colloidal state. The precipitate must be purified for it always contains adsorbed alkali.

Procedure. To a solution containing cobalt and nickel salts, add an excess of a 20 per cent solution of triethanolamine such that there are present 10 moles of the reagent for each mole of the metal. Add 0.01 N sodium carbonate solution until there are present 100 moles of sodium carbonate for each mole of the element. Nickel is completely precipitated when this solution is heated to boiling. Cobalt remains in solution.

To separate nickel and cobalt qualitatively, it is necessary only to add a slight excess of triethanolamine and a large excess of sodium carbonate. Nickel is precipitated on boiling, while cobalt yields a violet-purple solution.

When two drops of a 5 per cent cobalt chloride solution are added to an aqueous solution of triethanolamine that has been made alkaline with a drop of ammonium hydroxide, an intense purple-violet color is produced. This becomes blue on warming. This reaction has been used by Garelli and Tettamanzi[11] for the detection of triethanolamine. This reaction, however, may also be used to detect one part of cobalt in 15,000 parts of solution.

Separation of iron from cobalt and nickel. Kundert[22] has used triethanolamine for the precipitation of iron as a preliminary to the determination of nickel and cobalt in manganese ores. The separation is carried out as follows:

Procedure. Decompose a 10 g. sample of the manganese ore containing about 1.4 per cent iron by treating with concentrated hydrochloric acid. Evaporate on a hot plate and bake the residue. Moisten the residue with concentrated hydrochloric acid and boil with 50 ml. of water. Filter the hot solution, and wash the residue with hot water, adding the washings to the filtrate.

Heat the filtrate to 90° C., and nearly neutralize with ammonium hydroxide. Add to the hot solution a hot 10 per cent solution of triethanolamine until iron is completely precipitated, and the supernatant liquid is perfectly clear. Cool and filter, and wash the precipitate once with water. Transfer the precipitate to the original beaker with a minimum quantity of hot water. Dissolve in hydrochloric acid, again nearly neutralize with ammonium hydroxide, and repeat the precipitation with triethanolamine.

Combine the filtrates from the iron precipitations, warm, and precipitate nickel with dimethylglyoxime. To determine cobalt, add 3 ml. of concentrated hydrochloric acid to the combined filtrates, and evaporate to a volume of 100 ml. Add 15 ml. of glacial acetic acid, and precipitate cobalt by the addition of a hot acetic acid solution of α-nitroso-β-naphthol.

Determination of copper. The colorimetric determination of copper by using the blue complex with ammonia necessitates a careful control of conditions, and some advantage is claimed by replacing ammonia with one of its organic derivatives such as triethanolamine. This reagent is slightly more sensitive to low concentrations of copper, it has no odor, and it does not volatilize appreciably during the determination.[12]

Reagent. Dilute 127 g. of triethanolamine to 500 ml. in a volumetric flask. The resulting solution contains 25 per cent of the reagent by weight.

Procedure. To the copper solution add 0.5 ml. of concentrated nitric acid, and add the 25 per cent reagent solution until the blue color of the copper-triethanolamine complex appears, and then add 5 ml. of the reagent in excess. Dilute to 25 ml. in a volumetric flask, and determine copper by making transmission measurements with the aid of a photoelectric spectrophotometer.

Measurement is made at 625 mμ, and the transmission measurement is made on the basis that the transmission of the absorption cell containing water or the reagents (except copper) is 100.0 per cent. The absorption cell has a thickness of 1.000 ± 0.005 cm. and a capacity of 10 ml.

Detection of cadmium. Pozzi-Escot [21] has found that a mixture of equal molecular quantities of triethanolamine iodide and aniline is an excellent precipitant for cadmium.

Detection of molybdates and phosphates. When an excess of ammonium molybdate is added to a solution containing phosphoric acid or a phosphate, and the solution is then acidified with hydrochloric acid and treated with triethanolamine, a white precipitate forms which redissolves in an excess of the reagent with the formation of a deep blue coloration. The color disappears on heating but becomes more intense with an excess of ammonium molybdate or triethanolamine.[13] This reaction is sensitive to one part of phosphate in 40,000 parts of solution if sufficient reagent is added to give an alkaline reaction.

Procedure. Acidify 2-3 ml. of the molybdate solution with hydrochloric acid, and add the reagent slowly down the side of the test tube. A green ring forms at the junction of the two liquids, and this gradually becomes turbid with a blue precipitate forming. This is soluble in the reagent and partially soluble in water.

A similar reaction may be used to identify molybdates. In this case the phosphate is added to the solution to be tested along with triethanolamine.

A suitable reagent for precipitating phosphoric acid in the presence of arsenic acid is prepared as follows:

Reagent. Dissolve 15 g. of ammonium molybdate in 50 ml. of hot water; add an equal volume of pure triethanolamine. Mix with 20 ml. of 6 N nitric acid and 100 ml. of 10 per cent citric acid.

Procedure. Neutralize a solution containing the phosphate and arsenate to phenolphthalein, and add an excess of the reagent. Stir well and filter. Arsenic may be precipitated from the filtrate with magnesia mixture and ammonia. Phosphate is determined in the precipitate by dissolving in ammonia and precipitating with magnesia mixture.[14]

Very small quantities of molybdenum in the form of molybdic acid may be detected by adding a slight excess of triethanolamine and saturating the solution with hydrogen sulfide. A yellow-brown coloration appears in the presence of molybdenum. There is little interference from heavy metals.[15] When a solution containing molybdic acid and triethanolamine sulfide is allowed to evaporate spontaneously, the double sulfide separates and crystallizes as large needles or prisms. This reaction may be used for the microchemical detection of molybdenum.[17] Another microchemical test for molybdenum consists of the formation of triethanolamine phosphomolybdate. This compound is formed as well-defined cubic crystals when an acidified molybdenum solution is treated with sodium phosphate and triethanolamine.[16]

Detection of vanadium. When triethanolamine is added to a boiling acidified solution of a vanadate, the solution first becomes green, and then changes to a brilliant blue color. The color becomes brown in the presence of an excess of the reagent.[13]

Detection of iodine. Iodine dissolves in triethanolamine to form a colorless crystalline compound corresponding in composition to $HI \cdot N(C_2H_4OH)_3$.

Detection of mercuric chloride. When mercuric chloride is added to an acidified solution of iodine in triethanolamine, a yellow precipitate forms, which rapidly turns green. This precipitate is soluble in triethanolamine, and mercury is precipitated on heating.[13]

Detection of boric acid. A green coloration is obtained when copper sulfate is added slowly to a mixture of triethanolamine and boric acid. Other acids, such as hydrochloric, nitric, sulfuric, phosphoric, acetic, oxalic, tartaric, citric, benzoic and salicylic acids always give a blue coloration but never green. This reaction, therefore, while not very sensitive, is specific for boric acid.[18]

Detection of iron. When a solution of a ferric salt in triethanolamine is treated with potassium ferrocyanide, and hydrochloric acid is added dropwise until the solution is neutral, the color changes from red to violet and then to a deep blue. No precipitate forms, but upon further addition of the acid, a deep blue amorphous precipitate appears. Triethanolamine aids in the formation of the colloidal solution, since the blue liquid is simply a colloidal dispersion of prussian blue. Ferric ferrocyanide, obtained by the addition of potassium ferrocyanide to an acid solution of a ferric salt, also dissolves in triethanolamine to give a ruby-violet solution. Ferrous ferricyanide behaves similarly.[13]

Detection of antimony and bismuth. In the presence of iodine, bismuth and antimony salts react with triethanolamine to give brilliantly-colored, crystalline precipitates. The bismuth compound is scarlet in color and the antimony compound is golden-yellow.[18] The test is carried out by adding a few drops of a solution containing 8 g. of iodine in 100 ml. of triethanolamine to a solution of the bismuth or antimony salt that has been acidified with hydrochloric acid. The bismuth compound appears to be $HI \cdot N(C_2H_4OH)_3 \cdot BiI_3$, while the antimony compound is $NH_2C_2H_4OH \cdot SbI_3$.

Separation of antimony and tin. Most methods which have been used for the separation of antimony and tin depend upon the formation in acid solution of stannic complexes which are not decomposable by certain chemical reagents, in particular by hydrogen sulfide. While antimony is easily separated in the form of the sulfide, the determination of the tin presents a much more difficult problem. The use of triethanolamine makes possible an easy separation of the two metals in an alkaline solution.[19]

Procedure. If the tin is in the form of stannous salts, oxidize to the stannic state by adding bromine to the hydrochloric acid solution of the antimony and tin salts. To a definite volume of this solution, which contains approximately 0.3 g. of the mixed metals, add 300 ml. of a saturated solution of ammonium bicarbonate, and then a slight excess (about 15 ml.) of a 20 per cent solution of triethanolamine. The hydroxides dissolve immediately upon gentle heating and the stannic hydroxide then precipitates. Heat for an hour on a water-bath, filter, and wash with a solution containing 10 per cent of ammonium carbonate and 10 per cent of triethanolamine. A small portion of the antimony is retained by the precipitate, and this is removed by washing with warm 2-3 N hydrochloric acid. This treatment dissolves a small quantity of the tin, but this may be recovered by precipitating by the method described above. The two tin precipitates are collected on the same filter, dried, ignited and weighed as tin oxide.

Combine the filtrates containing antimony and make slightly acid with acetic acid. Dilute to 500 ml. and precipitate the antimony with hydrogen sulfide at 100° C. The precipitate is filtered through a Jena glass crucible, No. 1G4, ignited at 280° C. in a current of carbon dioxide and weighed as Sb_2S_3.

The results obtained using this method for separating antimony and tin are shown in Table 60.

TABLE 60.—SEPARATION OF ANTIMONY AND TIN

Used		Found	
Tin g.	Antimony g.	Tin g.	Antimony g.
0.009	0.17	0.009	0.171
0.092	0.17	0.092	0.171
0.184	0.085	0.186	0.084
0.184	0.017	0.185	0.017

Determination of hydrogen cyanide. Triethanolamine may be used with sodium sulfite as a stabilizing agent for the color formed in the action of hydrogen cyanide on a solution containing cupric ions and *o*-cresolphthalein in the colorimetric determination of hydrogen cyanide.[20]

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TRIETHYLENEDIAMINE

$C_6H_{12}N_2$ Mol. Wt. 112.16 Beil. Ref. IV, 249.

$$N{\equiv}(CH_2{-}CH_2)_3{\equiv}N$$

Use: Detection of bismuth.

Preparation: Triethylenediamine, along with other compounds, is prepared by the action of ammonia on ethylene bromide.[1]

Detection of bismuth. Triethylenediamine, in common with many nitrogenous organic compounds, yields an orange-red color when added to solutions of bismuth salts containing potassium iodide. This reagent appears to offer no advantage over other and more readily available compounds.[2]

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TRIMETHYLAMINE

C_3H_9N Mol. Wt. 59.11 Beil. Ref. IV, 43.

$N(CH_3)_3$

Use: Determination of aluminum and iron.

Trimethylamine is a colorless gas, which possesses a fish-like odor. It is very soluble in water, alcohol and ether. It is a strong base. It is usually obtained as a colorless aqueous solution possessing a strong ammoniacal odor.

Preparation: Heat 50 g. of ammonium chloride with 440 g. of 40 per cent formaldehyde solution in an autoclave to 110° C. The pressure gradually increases to about 35-40 atmospheres. When the pressure becomes constant allow the mass to cool. Convert the amine to the hydrochloride with hydrochloric acid, and evaporate to recover the salt. The free base is obtained by mixing the salt with powdered sodium hydroxide and warming gently.[1,2]

Separation of aluminum and iron. Iron is completely precipitated in the presence of aluminum by adding a large excess of a concentrated solution of trimethylamine to an aqueous solution containing iron and aluminum salts, and allowing to stand for 24 hours. The precipitated ferric hydroxide is washed with a trimethylamine solution until the washings leave no solid residue on evaporation. The ferric hydroxide is then dried and ignited to ferric oxide. Aluminum remains in solution.[3]

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UREA

Synonym: Carbamide, carbonyldiamide

CH_4ON_2 Mol. Wt. 60.06 Beil. Ref. III, 42.

$CO(NH_2)_2$

Use: Detection of antimony and tin.

Determination of aluminum, calcium, copper, gallium, iodide, nitrate and phosphorus.

Urea consists of white or colorless, odorless crystals which melt at 132-133° C. One gram of the solid dissolves in 1.1 ml. of water, 10 ml. of alcohol and 6 ml.

of methyl alcohol, but it is almost insoluble in chloroform and ether. The aqueous solution of the urea is neutral.

Preparation: Heat 50 g. of sodium or potassium cyanide in an iron dish until it begins to fuse, and then add gradually with stirring, 140 g. of red oxide of lead. Continue to heat until the mass fuses quietly, and then pour the dark colored liquid onto an iron plate and allow to cool. Separate the solidified material from the metallic lead and grind in a mortar. Pour 200 ml. of cold water onto the powdered mass immediately and allow to stand for 1 hour. Filter and wash with a little cold water. Add immediately to the filtrate a concentrated solution containing 25 g. of ammonium sulfate, and evaporate to dryness on a water-bath with occasional stirring. Allow the residue to cool and powder, and then extract the urea with alcohol by boiling on a water-bath under reflux. Add successively small quantities of alcohol until the extract leaves only a small residue when evaporated on a watch glass. Distill off most of the alcohol from the extract and allow the residue to crystallize.[1]

Determination of aluminum. Upon heating solutions of aluminum salts which contain sulfate ions and urea, aluminum is precipitated as the basic sulfate in a dense and easily filterable form. The favorable character of the precipitate is due to the slow and uniform increase in the pH of the solution, which is caused by the gradual hydrolysis of the urea. This is shown by the following equation:

$$(NH_2)_2CO + H_2O \rightarrow CO_2 + 2NH_3$$

There are several advantages in precipitating aluminum in this way: (a) The solution from which the precipitation occurs is homogeneous, since no reagents are added during the precipitation; (b) the precipitate formed in this way is much less bulky; and (c) the pH is easily controlled. The solubility of basic aluminum sulfate is about the same as aluminum hydroxide, and so results obtained by determining aluminum by precipitation as the basic sulfate are quite satisfactory. An amount of the basic sulfate equivalent to about 0.2 mg. of Al_2O_3 per liter dissolves at pH 6.5-7.5. Aluminum is also precipitated in the presence of selenate, succinate, formate, benzoate and phthalate, although precipitation as the basic sulfate appears to be the most satisfactory.[2]

In a sulfate solution, aluminum is quantitatively precipitated at pH 6.5-7.5 by boiling the solution gently for 1-2 hours after the first appearance of a turbidity. The necessary pH is obtained in a volume of 500 ml. by adding 4 g. of urea, 20 g. of ammonium chloride and 1 g. of ammonium sulfate. As the solution is boiled, the pH slowly rises due to the decomposition of urea. The residue obtained after ignition of the precipitate at 1200° C. contains only negligible quantities of sulfate. A single precipitation gives a good separation of 0.1 g. of aluminum from 1 g. of calcium, magnesium or manganese.[3]

If succinic acid is substituted for the sulfate, the complete precipitation of aluminum takes place at pH 4.2-4.6. The same quantities of urea and ammonium chloride which are recommended for the determination with sulfate are also used with succinic acid. About 4-5 g. of the latter acid is used. By this method a single precipitation serves to separate 0.1 g. of aluminum from 1 g. of calcium, barium, magnesium, manganese and cadmium, or a few mg. of aluminum from 1 g. of nickel or cobalt. If the aluminum oxide is ignited in hydrogen, the separation is excellent when 0.1 g. of aluminum and 1 g. of zinc are present. By a double precipitation, a good separation of 0.1 g. of aluminum from 1 g. of nickel, cobalt or zinc is obtained. If copper is present, it is necessary to provide a reducing agent to keep the copper in the cuprous state. Hydroxylamine is recommended for this purpose. Iron and aluminum are separated fairly well if the iron is reduced to the ferrous state. The following procedure is recommended.

Procedure. To a solution containing about 0.1 g. of aluminum, add hydrochloric acid until the mixture is slightly acid, and then add ammonium hydroxide until the solution becomes slightly turbid.

If the solution is originally acid, omit the addition of the hydrochloric acid and make slightly alkaline with ammonium hydroxide. Then clear the turbidity with dilute hydrochloric acid and add 1-2 drops in excess.

Add 4 g. of urea, 20 g. of ammonium chloride and 1 g. of ammonium sulfate. Dilute to 500 ml. and boil the solution gently for 1-2 hours. Filter the precipitate of basic aluminum sulfate, wash and ignite at 1200° C.

The results obtained in determining aluminum by the basic sulfate method are given in Table 61.

Willard and Tang[3] have studied the separation of aluminum from various metals by precipitating as the basic sulfate. Their results are given in Table 62.

The time of boiling a solution containing urea is important in obtaining the correct pH. Willard and Tang[2] studied the pH of a solution containing aluminum chloride equivalent to 2.0 g. of the metal, 4 g. of urea and 1 g. of ammonium sulfate in a volume of 500 ml. The pH at different intervals is given in Table 63.

Determination of gallium. By heating an aqueous solution of urea, the pH of the solution is slowly raised, and the final acidity controlled by the duration of the heating period. This fact is used to considerable advantage in the formation of precipitates which are produced by hydrolysis. The precipitate obtained by heating a gallium salt consists of the pure hydrated oxide at a pH of 8.5. In the presence of sulfate, however, considerable basic sulfate is precipitated at a pH of 3.3. The precipitation of gallium in 0.02 M ammonium sulfate is nearly complete at pH 4-4.5. Under these conditions only 0.2 mg. of gallium remains in 1 liter of solution after the precipitation.[4]

The following method is used for the determination of gallium, and for its separation from zinc, manganese and calcium.[5]

Procedure. To the solution containing the gallium salt, add a filtered solution of 3 g. of urea in 150-200 ml. of water. Dilute nearly to 500 ml., and add ammonium hydroxide dropwise until the solution is almost permanently turbid. Heat to incipient boiling and keep at that temperature until a sample of the solution shows a pH of 4-5.5. At this pH the solution is barely alkaline to methyl orange. Filter through a weighed porcelain filter crucible, wash with

TABLE 61.—DETERMINATION OF ALUMINUM BY BASIC SULFATE METHOD

Al_2O_3 Used g.	Al_2O_3 Found g.	Error Al_2O_3 mg.	Final pH of Solution
0.1913	0.1916	+0.3	7.08
0.1954	0.1956	+0.2	7.07
0.1960	0.1957	—0.3	7.03
0.1950	0.1954	+0.4	7.27
0.1915	0.1912	—0.3	6.77
0.1909	0.1907	—0.2	6.58
0.1941	0.1940	—0.1	7.09
0.1920	0.1917	—0.3	7.17
0.1920	0.1921	+0.1	6.94
0.1914	0.1913	—0.1	6.99

TABLE 62.—SEPARATION OF ALUMINUM BY BASIC SULFATE METHOD

Aluminum Used g.	Metal Added g.	Amount Present in Precipitate mg.
0.1	Ca 1.0	Trace
0.1	Mg 1.0	None
0.1	Ni 0.125	0.7
0.1	Co 0.125	1.0
0.1	Zn 0.125	13.6
0.1	Mn 1.0	0.1
0.1	Cd 0.125	0.4
0.1	Cu 0.125	7.3

TABLE 63.

Hours Heated	pH
0.66	6.5
1.5	7.1
2	7.5
2.5	7.8
3	8.0
4	8.2
6	8.4

cold water and ignite to 850° C. After weighing, transfer most of the oxide to an unglazed porcelain crucible and ignite for 1 hour at 1200° C. and again weigh. From the loss of weight, the corrected weight of the entire precipitate may be calculated.

The basic sulfate of gallium is not as insoluble as might be desired for a gravimetric determination, but it is less soluble than the corresponding hydroxide. Only about 0.1-0.2 mg. of Ga_2O_3 remains in 500 ml. of the filtrate.

The most troublesome feature of the gallium determination lies in the difficulty encountered in removing the precipitate from the beaker in which precipitation is carried out. Aluminum, chromium and iron interfere with this determination.

Elimination of nitrites. Many analytical procedures require the removal of nitrite to eliminate interference with subsequent operations. This removal is best effected by means of the reaction of nitrous acid with urea:

$$CO(NH_2)_2 + 2HNO_2 \rightarrow 2N_2 + CO_2 + 3H_2O$$

This use of urea is illustrated by the following examples:

(1) Nitrous acid invariably gives a rose color with brucine, thus causing interference in the determination of nitrates with this reagent. By adding urea, nitrite is destroyed, and the nitrate may be determined in the usual manner.[6]

(2) The presence of more than 1.0 p.p.m. of nitrite causes values for nitrate which are too high when determined by the phenolsulfonic acid method or the 1,5-naphtholsulfonic acid method. A study of these two methods indicates that the effect of nitrite can be overcome by treating with urea.[7]

(3) In the electrolytic determination of copper, the metal is best deposited from a nitric acid solution, but the formation of the nitrite ion during the process interferes with the complete separation of the copper. To eliminate this difficulty, the nitrite is removed by the addition of urea.[8]

(4) One of the methods used for the determination of iodide consists in the oxidation of the iodide to free iodine with sodium nitrite, and the titration of the liberated iodine with standard thiosulfate. When an excess of sodium nitrite is added to an iodide solution in an acid medium, the iodide is oxidized quantitatively according to the following equation:

$$2NO_2^- + 2I^- + 4H^+ \rightarrow 2NO + I_2 + 2H_2O$$

Before titrating the liberated iodine, however, it is necessary to remove both the excess nitrous acid and the nitric oxide formed in the reaction, since both of these substances interfere in the final determination. The elimination of these substances is easily accomplished by an addition of an excess of urea.

The above examples include only a few of the many possibilities, but they illustrate the manner in which urea may be used in analytical procedures.

Detection of antimony and tin. Antimony and tin salts react with urea in the presence of potassium iodide to give color reactions which are used for the detection of these metals. Gautier[9] has suggested that urea may be used to replace antipyrine in the well-known reaction for antimony and tin.

Determination of calcium. Urea is used for the precipitation of coarse crystals of calcium oxalate in the gravimetric determination of calcium. To do this, add ammonium hydroxide to a hot acid solution containing calcium and oxalate ions until calcium oxalate just begins to precipitate, and then add about 15 g. of urea. Keep the solution just below boiling for 20 minutes to 1 hour. The acid is slowly neutralized by the ammonia which is formed by the hydrolysis of urea.

Calcium oxalate crystals formed in this manner are coarse and easily filtered and washed.[13]

Determination of monocalcium phosphate. Whitaker and coworkers[10,11] have shown that urea reacts with monocalcium phosphate according to the equation:

$$Ca(H_2PO_4)_2 \cdot H_2O + CO(NH_2)_2 \rightarrow H_3PO_4 \cdot CO(NH_2)_2 + CaHPO_4 + H_2O$$

to yield urea phosphate and dicalcium phosphate. This reaction has been used as the basis for a method for determining monocalcium phosphate.[12] This procedure is based upon the fact that urea phosphate is soluble in alcohol while dicalcium phosphate is not. The determination requires three operations: (a) treatment of the sample with a large excess of urea to insure the completion of the reaction; (b) separation of the dissolved dicalcium phosphate by precipitating with alcohol; and (c) the determination of P_2O_5 in the resulting alcoholic solution of urea and urea phosphate.

Procedure. Use a sample containing at least 1 g. of $Ca(H_2PO_4)_2 \cdot H_2O$, and place in a 100-ml. volumetric flask. Add 50 ml. of a solution prepared by dissolving 90 g. of C.P. urea in 100 ml. of water and shake for four hours. Dilute to the mark, filter immediately through a dry filter, and discard the first few ml. Then to a 25-ml. aliquot of the filtrate, add 75-100 ml. of 95 per cent alcohol. Stir well, filter, and wash the precipitate with 300-350 ml. of alcohol. Dilute the combined filtrate and washings to 500 ml. with water, and use a 25-ml. aliquot of this solution for the final determination.

Evaporate to dryness, and then again evaporate to dryness with 5 ml. of hydrochloric acid and 25 ml. of nitric acid to destroy any organic matter. Repeat the evaporation with smaller quantities of acid if urea is still present. Then add 10 ml. of concentrated nitric acid, a little water, neutralize with ammonium hydroxide, and then make the mixture slightly acid with nitric acid. Adjust the volume to 75 ml. and determine P_2O_5 in the usual manner with ammonium molybdate. Calculate the quantity of monocalcium phosphate present in the original sample by reference to the above equation.

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VANILLYLIDENE BENZIDINE

Synonym: 3-Methoxy-4-hydroxybenzalbenzidine

$C_{20}H_{18}O_2N_2$ Mol. Wt. 318.34 Beil. Ref. XIII, 226(65).

$$HO(CH_3)C_6H_3—CH=N—C_6H_4—C_6H_4—NH_2$$

Use: Determination of tungsten and molybdenum.

Vanillylidene benzidine is obtained as a yellow crystalline solid from benzene. It begins to sinter at 170° C., melts at 181° C., and consists of a clear liquid at 184-185° C. It dissolves in acetic acid with a red color, and in alcohol to form a yellow solution.

Preparation: Dissolve 2 g. of vanillin in a hot mixture of 25 ml. of alcohol and 50 ml. of water and add 2.4 g. of benzidine dissolved in 58 per cent alcohol. A bright yellow precipitate forms. Allow to stand for a time, filter, wash, and dry, and then purify by recrystallization from hot benzene.[1]

Determination of tungsten. Hovorka [2,3] has studied the use of several condensation products of aldehydes with benzidine for the determinaiton of tungsten. Among these, vanillylidene benzidine has proved the most useful. An acetic acid solution of vanillylidene benzidine gives with tungstates a reddish-brown precipitate which may be converted into tungstic oxide by ignition. Precipitation is quantitative. The tungsten compound is somewhat soluble in water, and so it is necessary to use a dilute solution of the precipitating agent for washing the precipitate.

Tungsten is determined with this reagent in much the same manner as with benzidine. The former reagent possesses the advantage of giving a less soluble precipitate and a characteristic color reaction. The composition of the precipitate is not constant. As with the analogous benzidine compound, it is without doubt a vanillylidene benzidine tungstate, but contaminated by other substances. The quantity of the contaminating substances is somewhat variable. They may be neglected, however, in the determination since on ignition of the precipitate to tungstic oxide they are completely volatilized.

Procedure. Dissolve 0.006-0.4 g. of the alkali tungstate in 20-80 ml. of water and heat the solution to boiling. Remove the flame and add an excess of a 3 per cent solution of vanillylidene benzidine in 50 per cent acetic acid (5-25 ml.). The supernatant liquid should be brown to reddish-brown to show an excess of the precipitant. Allow the mixture to stand for 3-5 hours, filter, and wash the precipitate with 30-100 ml. of a solution prepared by diluting 10 ml. of the reagent to 400-500 ml. Ignite and weigh as WO_3.

Tungsten may also be precipitated from a cold solution by adding to an alkali tungstate about 10 ml. of 0.1 N sulfuric acid and then precipitating in the cold with an excess of the 3 per cent solution of vanillylidene benzidine in 50 per cent acetic acid. Allow to stand for about 15 minutes, filter, and wash as above, and convert to WO_3 by ignition.

Precipitation from hot solutions gives a coarser grained precipitate which is easy to filter. The results obtained using this method are shown in Table 64.

TABLE 64.—DETERMINATION OF TUNGSTEN WITH VANILLYLIDINE BENZIDINE
(precipitation from hot solution)

WO_3 Used g.	WO_3 Found g.	Error g.
0.0177	0.0176	—0.0001
0.0726	0.0725	—0.0001
0.1948	0.1946	—0.0002
0.2315	0.2302	—0.0013
0.0055	0.0056	+0.0001
0.0090	0.0093	+0.0003
0.0104	0.0106	+0.0002
0.0181	0.0182	+0.0001
0.0271	0.0271	—0.0000
0.0313	0.0316	+0.0003

Determination of molybdenum. Solutions of alkali molybdates react with acetic acid solutions of vanillylidene benzidine to give a voluminous reddish-brown precipitate of variable composition, but which yields MoO_3 upon ignition. Precipitation is accomplished in practically the same way as in the determination of tungsten, but with molybdenum the solution must be kept boiling while adding the reagent, and must be boiled for at least 30 seconds after the reagent has been added. Most results obtained by this method are satisfactory.[4]

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1. A. A. Torrey and E. D. Clarke, *J. Am. Chem. Soc.* **31**, 583 (1909).
2. V. Hovorka, *Chem. Listy.* 33, 212-16 (1939); *C.A.* **33**, 6194 (1939).
3. V. Hovorka, *Collection Czechoslov. Chem. Commun.* 10, 518-26 (1938); *C.A.* **33**, 1624 (1939).
4. V. Hovorka, *Collection Czeckoslov. Chem. Commun.* **10**, 527-33 (1939); *C.A.* **33**, 1624 (1939).

XYLIDINE

Synonym: Dimethylaminobenzene

$C_8H_{11}N$ Mol. Wt. 121.18 Beil. Refs. XII, 1101, 1103, 1107, 1111, 1131, 1135.

Uses: Detection of gold, hydrogen peroxide, iridium, nitrite, osmium, palladium and platinum.

Determination of cerium, lanthanum, nitrites, praseodymium, neodymium, thorium and zirconium.

There are six isomeric xylidines. These are prepared by reduction of the corresponding nitro compounds. All except *o*-4-xylidine are liquids above 20° C. The sp. gr. is 0.97-0.99 and the boiling points lie between 213° C. and 226° C. These amines are sparingly soluble in water, but are soluble in alcohol and form more or less soluble salts with strong mineral acids.

Detection of the platinum metals. Whitmore and Schneider[1] have investigated the use of some of the isomeric xylidine hydrochlorides for the microchemical detection of the platinum metals. Their results are shown in Tables 65 and 66.

TABLE 65.—REACTIONS OF *p*-XYLIDINE WITH THE PLATINUM METALS

Test Material	Description
$RuCl_3$	No apparent reaction.
$RhCl_3$	No apparent reaction.
$PdCl_2$	A dense, bright-yellow, amorphous precipitate forms immediately.
Na_2OsCl_6	On standing a short time some very irregular, bright-yellow crystalline structures develop near the edge of the drop.
$IrCl_4$	A scant, purple, amorphous precipitate forms immediately. Color gradually changes to green.
H_2PtCl_6	Some very pale-yellow, flat plates of considerable size develop throughout the drop gradually. These occur singly and in clusters.
$AuCl_3$	A dense, purple, amorphous precipitate forms immediately. The color gradually changes to green.

TABLE 66.—REACTIONS OF *m*-XYLIDINE WITH THE PLATINUM METALS

Test Material	Description
$RuCl_3$	No apparent reaction.
$RhCl_3$	No apparent reaction.
$PdCl_2$	A dense, yellow, amorphous precipitate forms gradually.
Na_2OsCl_6	A few bright-yellow, irregular structures develop at the edge of the drop after standing a short time. No definite crystalline structures could be recognized.
$IrCl_4$	A scant, purple, flocculent precipitate forms gradually.
H_2PtCl_6	Many, slender, bright-yellow, needle-shaped crystals develop immediately. These are pointed at both ends and of enormous length, some extending nearly across the drop.
$AuCl_3$	A very dense, purple, amorphous precipitate forms immediately.

The results given in these tables were obtained by the use of a saturated solution of *p*-xylidine hydrochloride and a 10 per cent solution of *m*-xylidine hydrochloride. These reagents were added to a 2 per cent solution of the metal salts.

Precipitation of metals. Jefferson[2] has found that xylidine may be used as a precipitant for zirconium, thorium, cerium, lanthanum, neodymium and praseodymium.

Detection and determination of nitrite. The following reaction is used for the detection of nitrite:[3]

Reagents. *Xylidine acetate solution:* Dissolve 1.81 g. of xylidine acetate in 10 ml. of acetic acid and dilute to 1 liter.

β-Naphthol solution: Dissolve 2.65 g. of β-naphthol and 10 g. of sodium hydroxide in sufficient water to make 1 liter.

Procedure. Place 50 ml. of the sample suspected of containing nitrite in a Nessler tube and add 1 ml. of the xylidine acetate solution. Shake and allow the mixture to stand for 5 minutes and then add 5 ml. of the β-naphthol solution. An orange-red color is formed if nitrite is present. This color is also used for the colorimetric determination of nitrite. This reaction is sensitive to 2.84×10^{-6} g. of sodium nitrite per ml.

Detection of hydrogen peroxide. Ilosvay[4] has used xylidine in a reagent for the detection of hydrogen peroxide.

Reagent. Dissolve about 5 drops of xylidine and 0.03 g. of potassium dichromate in a liter of water. This reagent is yellow in color.

Procedure. Mix 5 ml. of the reagent with 5 ml. of the solution to be tested, and acidify with a few drops of 5 per cent oxalic acid. On standing a reddish-violet coloration appears if hydrogen peroxide is present.

1. W. F. Whitmore and H. Schneider, *Mikrochemie.* **17**, 279-319 (1935).
2. A. M. Jefferson, *J. Am. Chem. Soc.* **24**, 540-62 (1902).
3. F. C. Alzamora, *Bol. soc. quim. Peru.* **5**, 240-1 (1939); *C.A.* **34**, 4010 (1940).
4. L. Ilosvay, *Ber.* **28**, 2029 (1895).

CHAPTER X

QUATERNARY AMMONIUM COMPOUNDS

A number of quaternary ammonium hydroxides and salts have been used with considerable advantage as precipitants for antimony, bismuth, cadmium, magnesium, zinc and other metals. They have also been used as microchemical reagents for the platinum metals. These compounds are:

CHOLINE

Synonym: Sincaline, bilineurine, amanintine, gossypine, vidine, bursine, luridine, fagine, trimethyl-β-hydroxyethylammonium hydroxide

$C_5H_{15}O_2N$ Mol. Wt. 121.18 Beil. Ref. IV, *277*(425).

$$HO—CH_2—CH_2(CH_3)_3NOH$$

Use: Determination of cobalt, ferrocyanide and potassium.

Detection of cobalt and ferrocyanide.

Choline is found in nature in many plants and animal organs, such as in bile, brain, yolk of eggs, hops and belladonna. It is the basic constituent of lecithin. It is a colorless viscous strongly alkaline liquid. It must be stored in tightly closed containers as it adsorbs carbon dioxide from air. It is very soluble in water and alcohol, but is insoluble in ether.

Preparation: Extract the yellows of 24 eggs two times with 1.5 liters of ether, and extract the insoluble residue two times with hot alcohol. Evaporate ether and alcohol extracts, and heat the residue with a solution of 50 g. barium hydroxide in a liter of methyl alcohol. Precipitate the excess barium hydroxide by means of a stream of carbon dioxide and filter. Evaporate the filtrate to dryness on a water bath and dissolve the residue in water. Filter the aqueous solution, and again evaporate to dryness. Dissolve the residue in alcohol. Filter, and precipitate the alcoholic solution with an alcoholic solution of mercuric chloride. Filter off the precipitate, wash, and dissolve in hot water. Pass hydrogen sulfide through the solution to precipitate the mercury as mercuric sulfide. Filter, and evaporate to dryness. Evaporate the residue with dilute hydrochloric acid, and again dissolve in alcohol. Evaporate the alcohol, dissolve the residue in water, and precipitate choline with an alcoholic cadmium chloride solution.

Detection and determination of cobalt and ferrocyanide. When sodium ferrocyanide is added to a mixture of a cobalt salt and choline hydrochloride in an aqueous solution, an emerald-green color develops immediately. This reaction may be used for the detection and determination of small quantities of cobalt and ferrocyanide. Hibbard,[5] for example, has made this reaction the basis for a method of determining cobalt in soil.

Determination of potassium. One of the standard methods for determining potassium in blood serum and in solutions of ashed biological materials has been based upon the separation of potassium by precipitation as potassium cobaltinitrite. This method, originally proposed by Kramer and Tisdall,[1] has never been entirely satisfactory due to the empirical nature of the precipitate which is formed. The formula usually assigned to this compound is $K_2NaCo(NO_2)_6 \cdot H_2O$, although this apparently does not represent the composition in all cases. The washed precipitate in the procedure of Kramer and Tisdall is finally oxidized by a standard potassium permanganate solution, but the factor relating the quantity of permanganate to potassium has varied among different analysts. Accordingly, Eden[2] has used a procedure based upon a reaction originally observed by Jacobs and Hoffmann[3] for the indirect determination of potassium after precipitation as potassium cobaltinitrite. The method of Jacobs and Hoffmann depends upon the measurement of the cobalt content of the precipitated potassium cobaltinitrite colorimetrically by means of the emerald-green color which is produced when a cobalt solution is allowed to react with choline hydrochloride and sodium or potassium ferrocyanide. This method is said to be as accurate as those using chloroplatinic acid.[4] The following procedure is described by Eden:[2]

Reagents. *Sodium cobaltinitrite solution:* Dissolve 120 g. of sodium nitrite in 180 ml. of water, and pour 210 ml. of this solution into a solution prepared by dissolving 12.5 ml. of glacial acetic acid and 25 g. of $Co(NO_3)_2 \cdot 6H_2O$ in 50 ml. of water. Aspirate air through the mixture until the fumes of the oxides of nitrogen have disappeared, and then allow to stand overnight in a refrigerator. Finally filter through Whatman No. 40 paper. Store in a cold place and filter each time before using.

Choline hydrochloride solution: This reagent is a 10 per cent aqueous solution which is diluted to a 1 per cent solution just before using. The concentrated solution must be stored in a cold place.

Serum wash fluid: Precipitate potassium cobaltinitrite by adding potassium chloride to a solution of sodium cobaltinitrite. Wash in a centrifuge with water, and form a saturated solution by shaking the precipitate with water and allowing to stand overnight. Separate the excess precipitate in the centrifuge and use the supernatant liquid for washing.

Standard potassium solution: Dissolve 0.4457 g. of dried potassium sulfate in water and dilute to 1 liter. One ml. of this solution contains 0.20 mg. of potassium.

Standard cobalt solution: Dry cobalt sulfate in an oven at 160° C. for 6 hours. The residue consists of $CoSO_4 \cdot H_2O$. Dissolve 0.485 g. of this product in a liter of water containing 5 ml. of N sulfuric acid. One ml. of this solution contains 0.165 mg. of cobalt, which is approximately the same quantity of cobalt contained in the precipitate from 1 ml. of the standard potassium solution.

Procedure. Place an aliquot of the solution to be analyzed containing 0.1-0.3 mg. of potassium, or 1 ml. of serum to be analyzed, in a graduated 15-ml. centrifuge tube. Add 0.5 ml. of a 50 per cent sodium nitrite solution. Mix well, dilute to 4 ml., again mix, and add 2 ml. of the sodium cobaltinitrite reagent dropwise from a buret. Mix well, allow to stand for one hour, and centrifuge for 10 minutes at approximately 2500 r.p.m. When serum is used, remove the supernatant liquid with a small siphon having a fine, slightly upturned tip, and add 2 ml. of the serum wash fluid and again centrifuge for 5 minutes. Remove the supernatant liquid as completely as possible with a siphon and wipe the mouth and upper portion of the tube with a clean cloth which has been moistened with 70 per cent alcohol. Break up the precipitate with 5 ml. of 70 per cent alcohol. Centrifuge for 5 minutes and remove the supernatant liquid as before. Repeat the washing with a second 5-ml. portion of 70 per cent alcohol after disintegrating the precipitate and washing down the sides. Remove the supernatant liquid completely, and suspend the precipitate in 3.0-3.5 ml. of water. Immerse the tube in a beaker of boiling water. Stir until the precipitate is all dissolved, and then cool.

Add 1 ml. of 1 per cent choline hydrochloride solution and 1 ml. of a freshly prepared 2 per cent solution of potassium ferrocyanide. Dilute to 6 ml. and mix well. Compare the resulting green color with that of standard solutions of cobalt sulfate prepared as described above. The cobalt solution must be standardized against the standard potassium sulfate solution by using the same procedure as that described in the determination. The standards are prepared by diluting 1 ml. of the standard cobalt solution to 4 ml., then adding 1 ml. of the choline hydrochloride solution and 1 ml. of a freshly prepared 2 per cent potassium ferrocyanide solution.

The color of the standard and unknown solution may be compared visually, or in a Pulfrich photometer equipped with 1-cm. cells against a blank containing 1 ml. each of choline hydrochloride solution and potassium ferrocyanide solution diluted to 6 ml. A S57 filter is the most suitable. Over the range of 0.05-0.35 mg. of potassium in the aliquot used, the relation between extinction and potassium is linear, and the straight line passes through the origin. Factors given for 0.20 mg. of potassium are:

$$E = 0.265 \text{ with a S 47 filter}$$

$$E = 0.345 \text{ with a S 57 filter}$$

$$E = 0.545 \text{ with a S 61 filter}$$

When analyzing serum (1 ml.), $E \times 57.97$ = mg. K per 100 ml. with filter S 57. Table 67 shows the accuracy of this method:

TABLE 67.—RESULTS WITH PURE POTASSIUM SULFATE

K Added mg.	K Found mg.
0.050	0.045
0.100	0.098
0.150	0.159
0.200	0.207
0.250	0.257
0.300	0.300
0.350	0.343
0.400	0.394

Morris and Gerdel[4] have used a similar method for determining potassium in plant material.

1. B. Kramer and F. F. Tisdall, *J. Biol. Chem.* 46, 339 (1921).
2. A. Eden, *Analyst.* **68**, 167-71 (1943); *C.A.* 37, 4984 (1943).
3. H. R. D. Jacobs and W. S. Hoffmann, *J. Biol. Chem.* 93, 685-91 (1931); *C.A.* **26**, 752 (1932).
4. V. H. Morris and R. H. Gerdel, *Plant Physiol.* **8**, 315-9 (1933).
5. P. L. Hibbard, *Ind. Eng. Chem., Anal. Ed.* 10, 615-8 (1938).

PHENYLBENZYLDIMETHYLAMMONIUM CHLORIDE

$C_{15}H_{18}NCl$ Mol. Wt. 247.75

$$C_6H_5(C_6H_5CH_2)(CH_3)_2NCl$$

Use: Detection of platinum.

This reagent is a colorless crystalline solid melting at 110° C. It is soluble in water but insoluble in ether.

Preparation: Mix equal molecular quantities of benzyl chloride and dimethylaniline and allow the mixture to stand at ordinary temperature until the mass crystallizes. Wash with ether and recrystallize the residue from 95 per cent alcohol to obtain colorless crystals.[1,2]

Detection of platinum. Phenylbenzyldimethylammonium chloride is used to precipitate platinum in a systematic scheme of qualitative analysis. A few drops of a 10 per cent aqueous solution of reagent added to same quantity of a solution 4 N in hydrochloric acid, and containing platinum, gives a distinct buff colored precipitate with 25γ of platinum.[3] The insoluble platinum compound is presumably

$$[(CH_3)_2(C_6H_5)(C_6H_5CH_2)N]_2PtCl_6$$

Other reactions obtained with the reagent and various cations are given in Table 68:

TABLE 68.

Metal	Sensitivity	Reaction	Behaviour When Heated in Boiling Water
Palladium	25 γ	Light brown precipitate	Dissolves
Mercury	250 γ	White precipitate	Dissolves
Rhodium	250 γ	Pale violet precipitate	Dissolves
Gold	500 γ	Yellow precipitate	Decomposes
Iridium	125 γ	Red brown precipitate	Reduced bulk
Platinum	25 γ	Buff precipitate	Unaffected

1. W. Michler and A. Gradmann, *Ber.* **10**, 2078 (1877).
2. J. L. Maynard, H. H. Barber, and M. C. Sneed, *J. Chem. Ed.* **16**, 77 (1939).
3. C. C. Miller and A. J. Lowe, *J. Chem. Soc.* **143**, 1258-66 (1940); *C.A.* **35**, 707-8 (1941).

PHENYLTRIMETHYLAMMONIUM IODIDE

$C_9H_{14}NI$ Mol. Wt. 263.12

$C_6H_5(CH_3)_3NI$

Use: Determination of cadmium.

Preparation: Dissolve 13 ml. of dimethylaniline and 7.5 ml. of methyl iodide in 50 ml. of chloroform and allow the mixture to stand for several days. Filter, wash well with chloroform, and allow to dry. The compound melts at 228-234° C.

Determination of cadmium. Pass and Ward[1,4] have used phenyltrimethylammonium iodide as a reagent for the determination of cadmium. The following procedure, which may be used in the presence of other metals, has been suggested:

Procedure. Add a few drops of sulfurous acid to a solution of metals contained in 50 ml. of 2 N sulfuric acid and boil, and then add a few clean iron nails. Heat at just below the boiling point for one hour, adding water occasionally to maintain the volume at approximately 50 ml. Filter through a sintered glass crucible containing a piece of iron wire, and then wash well with cold water. To the filtrate, add 3 g. of potassium iodide and 25-30 ml. of a 2.5 per cent aqueous solution of the reagent. Allow to stand six hours and filter through a Gooch or sintered glass crucible. Wash with 5 successive portions of about 5 ml. each of a solution prepared by dissolving 1 g. of potassium iodide and 1 g. of the reagent in 200 ml. of water. Wash and dry by suction. Transfer the precipitate and the asbestos to the beaker in which the original precipitation was carried out, and thoroughly mix with 20 ml. of 2 N ammonia solution. Collect the asbestos and the cadmium compound in a Gooch crucible and wash with 2 N ammonia and water. Transfer the filtrate to a volumetric flask and rinse with 2 N hydrochloric acid in such quantity (about 100 ml.) that its concentration at the end of the titration is approximately normal. Then add 5 ml. of 10 per cent potassium cyanide solution and a little starch indicator. Titrate with

M/40 potassium iodate until the blue color which first appears turns to a reddish-violet, and then finally disappears.

$$1 \text{ ml. M/40 } KIO_3 \equiv 1.405 \text{ mg. Cd.}$$

Not more than 0.05 g. cadmium can be determined in this way. The calculation is based on the following relationships:

$$[C_6H_5(CH_3)_3N]_2CdI_4 \rightarrow 4NH_4I \rightarrow 4HI$$
$$2HI + HIO_3 + 3HCN \rightarrow 3ICN + 3H_2O$$

Kiba [2,3] has used this method for the determination of cadmium, and reports an accuracy of approximately 0.3 per cent.

1. A. Pass and A. M. Ward, *Analyst.* **58**, 667-72 (1933); *C.A.* **28**, 66-7 (1934).
2. T. Kiba, *J. Chem. Soc. Japan.* **59**, 583-5 (1938); *C.A.* **32**, 5726 (1938).
3. T. Kiba, *J. Chem. Soc. Japan.* **59**, 577 (1938); *C.A.* **32**, 5726 (1938).
4. K. Heller and F. Machek, *Mikrochemie.* **19**, 147-61 (1936).

TETRACETYLAMMONIUM HYDROXIDE

$C_{64}H_{133}ON$ Mol. Wt. 932.70

$(C_{16}H_{33})_4NOH$

Use: Detection and determination of bismuth.

Tetracetylammonium iodide is obtained as a white, crystalline powder, which is oily to the touch. After several crystallizations from ether, the compound melts at 80° C.

Preparation: Tetracetylammonium iodide is prepared by passing a stream of ammonia gas into cetyl iodide at a temperature of 200° C. The quarternary salt is separated from other products of the reaction by virtue of its slight solubility in ether. It is insoluble in petroleum ether; and, unlike tricetylamine, is moderately soluble in alcohol.[2]

Detection and determination of bismuth. Tetracetylammonium hydroxide reacts with bismuth salts in the presence of potassium iodide to give an insoluble red compound, having the formula $(C_{16}H_{33})_4NI \cdot BiI_3$. This reaction has been used by Girard and Fourneau [1-4] for the detection and determination of bismuth. Certain oxidizing agents such as ferric iron interfere with the test, but the interference due to iron is eliminated by adding a solution containing formic acid, ammonium formate, potassium iodide and sodium sulfite. This reagent is prepared by dissolving 200 g. of sodium formate, 30 g. of potassium iodide, 5 g. of crystalline sodium sulfite and 5 ml. of formic acid in sufficient water to make 1 liter of solution. If a small volume of a benzene solution of tetracetylammonium hydroxide is mixed with a dilute aqueous solution containing bismuth and potassium iodide, a red coloration appears at the junction of the two liquids, and the red compound passes into the benzene layer. The extraction is practically complete, and bismuth may be determined with a fair accuracy by comparing the color of the benzene extract with that of a similar extract obtained using a standard bismuth solution.

The benzene solution of the reagent is prepared as follows: Dissolve 10 g. of the quaternary iodide in 250 ml. of hot, pure benzene. Wash the solution by agitating with 10-20 ml. of a sodium hydroxide solution. Repeat the washing a second time to remove all iodine. Decant the benzene solution, dilute to 2 liters, and add 10 drops of acetic acid. Treat with decolorizing charcoal, filter, and store in clean, dark bottles.

1. A. Girard and E. Fourneau, *Compt. rend.* **181**, 610-11 (1925).
2. A. Girard and E. Fourneau, *Bull. soc. chim.* **37**, 1669-73 (1925).
3. A. Girard and E. Fourneau, *Repert. pharm.* **36**, 353-4 (1925); *C.A.* **20**, 725 (1926).
4. G. Gutzeit, *Helv. Chim. Acta.* **12**, 713 (1929).

TETRAETHYLAMMONIUM BROMIDE

$C_8H_{20}NBr$ Mol. Wt. 210.16 Beil. Ref. IV, 104.

$N(C_2H_5)_4Br$

Use: Detection of gold, iridium, osmium, palladium, platinum, rhodium and ruthenium.

Tetraethylammonium bromide is a crystalline solid which dissolves readily in chloroform and in alcohol.

Preparation: Tetraethylammonium bromide is prepared by the action of ethyl bromide on triethylamine.

Detection of platinum metals. Whitmore and Schneider[1] have studied the reaction of tetraethylammonium bromide with salts of the platinum metals. The results obtained by adding a solid fragment of the reagent to a drop of a 1 per cent solution of the material to be tested are given in Table 69, which is taken directly from the work of Whitmore and Schneider.

TABLE 69.—REACTIONS OF THE PLATINUM METALS

Test Material	Description
$RuCl_3$	As drop evaporates a great number of deep red, three leaved, rosette-like forms develop near the circumference.
$RhCl_3$	As drop evaporates some small, slender, spindle-shaped crystals appear near the circumference; also quite a number of radiating clusters of flat prisms appear.
$PdCl_2$	A dense, red, granular precipitate forms immediately around the test particle. There then appear in this precipitate many large aggregates made up of flat yellow forms. Around the edge of the precipitate many deep red crystals in the form of truncated pyramids develop.
Na_2OsCl_6	Many, small bright-yellow, octahedra form around the test particle and throughout the drop.
$IrCl_4$	Many, deep red, small, and rather poorly formed octahedra developed around the reagent particle.
H_2PtCl_6	Many, small bright-yellow, octahedra form around the test particle and throughout the drop.
$AuCl_3$	A dense, reddish-brown precipitate formed. At the edge of this precipitate, some bright yellow hexagonal plates appear.

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[1] W. F. Whitmore and H. Schneider, *Mikrochemie*, **17**, 279-319 (1935).

TETRAETHYLAMMONIUM CHLORIDE

$C_8H_{20}NCl$ Mol. Wt. 165.71 Beil. Ref. IV, 104.

$N(C_2H_5)_4Cl$

Use: Detection of antimony and bismuth.

Determination of gold.

Tetraethylammonium chloride is a crystalline solid which dissolves readily in water, alcohol, acetone and chloroform.

Preparation: Tetraethylammonium chloride is prepared by the action of ethyl chloride on triethylamine.

Detection of antimony and bismuth. Tetraethylammonium chloride is used as a microchemical reagent for the detection of small quantities of antimony and bismuth.[1] The addition of a little solid potassium iodide and a concentrated solution of tetraethylammonium chloride to a solution containing the antimonic ion causes the formation of purple hexagonal plates. This compound has the formula $(C_2H_5)_4NI \cdot SbI_4$. With trivalent antimony, yellow anisotopic crystals are formed. This compound is $3(C_2H_6)_4NI \cdot 2SbI_3$. Amber triangular tablets corresponding in composition to $3(C_2H_5)_4NI \cdot 2BiI_3$ are formed with bismuth salts.

Procedure. To the residue obtained by the evaporation of a nitric acid solution of the material to be tested, add a little 3 N hydrochloric acid and a crystal of potassium iodide. Note the formation of any significant precipitate which would indicate the presence of silver, mercury, lead, copper, selenium, tellurium or iodine, or any color change which would indicate bismuth, antimony or arsenic. Then add a drop of a fairly concentrated solution of tetraethylammonium chloride and observe the crystalline precipitate which is formed in the presence of antimony or bismuth.

Oxidizing agents such as cupric, ferric and arsenate ions interfere by liberating free iodine, which may yield yellow crystals with the reagent. Potassium sulfite reduces free iodine without reducing the antimony or bismuth, unless the solution is heated.

Determination of gold. Gold is precipitated quantitatively as a canary-yellow compound by the addition of tetraethylammonium chloride to solutions of gold salts. The precipitate cannot be dried and weighed, but must be ignited to metallic gold. Since the gold precipitate is free of platinum and palladium, Maynard[2] has used tetraethylammonium chloride for the determination of gold in dental alloys:

Procedure. Dissolve about 0.5-0.7 g. of the dental alloy in aqua regia and free the solution from silver, iridium and tin. Then precipitate the gold with sulfur dioxide. Filter, wash thoroughly with hot 1 per cent hydrochloric acid, and dissolve the gold in 20 ml. of dilute aqua regia. Filter off any paper pulp and wash with hot 1 per cent hydrochloric acid. Evaporate the filtrate to a volume of 2-3 ml., and add 5 ml. of concentrated hydrochloric acid. Again evaporate to 3 ml. Dilute to 20 ml., or 10 ml. if less than 10 mg. of gold is present, and add a suitable quantity of a 15 per cent aqueous solution of tetraethylammonium chloride. Four ml. of the reagent is used for each 0.1 g. of sample.

Allow the mixture to stand 15 minutes and filter. Wash four times with 5-ml. portions of the 15 per cent solution of the reagent, and transfer the paper and precipitate to a beaker. Cover with 35 ml. of a freshly prepared 20 per cent solution of glucose to which 2 g. of sodium hydroxide has been added, and boil for 1 minute. Add an equal volume of water and decant the liquid through a filter. To the filter paper and the gold add 25 ml. of hydrochloric acid and boil until the paper is disintegrated. Add an equal volume of water and filter through the same paper used for the decantation. Wash with hot water, dry at 120° C., and ignite in a porcelain crucible.

1. F. T. Jones and C. W. Mason, *Ind. Eng. Chem., Anal. Ed.* **8**, 428-31 (1936); *C.A.* **31**, 64 (1937).
2. J. L. Maynard, *Ind. Eng. Chem., Anal. Ed.* **8**. 368-9 (1936); *C.A.* **30**, 7484 (1936).

TETRAETHYLAMMONIUM HYDROXIDE

$C_8H_{21}ON$ Mol. Wt. 147.26 Beil. Ref. IV, 103.

$N(C_2H_5)_4OH$

Use: Determination of lithium, magnesium, potassium and sodium.

Tetraethylammonium hydroxide is marketed only in the form of an aqueous solution. The free base is known only in solution or as the solid hydrate. The tetrahydrate melts at 49-50° C., and the hexahydrate melts at 55° C. The free base decomposes on boiling. It is a very stronge base and readily absorbs carbon dioxide from the air. The aqueous solution is colorless, odorless and has a bitter caustic taste. Store in a tightly closed bottle.

Preparation: Dissolve 11.5 g. of potassium hydroxide in 92 g. of methyl alcohol and mix with 33.9 g. of tetraethylammonium chloride dissolved in 33.9 g. of methyl alcohol. Allow the mixture to stand for 1 hour and filter through asbestos. Filter quickly and transfer the filtrate to a large distilling flask. Add 100 ml. of water and remove a part of the water and methyl alcohol by distilling under reduced pressure at 50° C. Distill for about 3 hours and place the residue in a vacuum desiccator containing phosphorus pentoxide, and allow to stand several days. Recover crystals of the hydrate by filtration.[1]

Determination of magnesium. Borgstrom[2] has investigated the use of a number of bases for the quantitative precipitation of magnesium hydroxide. Tetraethylammonium hydroxide may be used for this purpose, but it appears to be less satisfactory than piperidine, sodium hydroxide or tetramethylammonium hydroxide.

Determination of sodium, potassium and lithium. Zlotowski and Kolthoff[3] recommend tetraethylammonium hydroxide as a more suitable supporting electrolyte in the polarographic determination of the alkali metals than the tetramethyl derivative. A solution of tetraethylammonium hydroxide is allowed to stand for 5-10 days and filtered before use. Potassium and sodium may be determined polarographically with an accuracy of 3 per cent in a 50 per cent ethyl alcohol medium. The concentration of the tetraethylammonium hydroxide is made at least 50 times that of the alkali ions. Lithium is best determined in an 80 per cent alcohol medium.

1. D. C. Crichton, *J. Chem. Soc.* **91**, 1794 (1907).
2. L. Borgstrom, *Hyllningsskrift tillagnad Ossian Aschan.* 118 (1920); *C.A.* **16**, 2091 (1922).
3. I. Zlotowski and I. M. Kolthoff, *Ind. Eng. Chem., Anal. Ed.* 14, 473-4 (1942); *C.A.* **36**, 4437 (1942).

TETRAMETHYLAMMONIUM HYDROXIDE

$C_4H_{13}ON \cdot 5H_2O$ Mol. Wt. 181.23 Beil. Ref. IV, 50.

$N(CH_3)_4OH$

Use: Determination of lithium, magnesium, potassium, and sodium.

Tetramethylammonium hydroxide is usually marketed in a 10 per cent aqueous solution. The free base is known only in solution, or as solid pentahydrate which is obtained as colorless deliquescent needles which melt at 63° C. The compound is a very strong base and rapidly absorbs carbon dioxide from air. The reagent should be preserved in a tightly stoppered bottle.

Preparation. *Tetramethylammonium chloride:* Dissolve 9.2 g. of trimethylamine (for preparation see reference 1) in 50 g. of absolute ether, and transfer the solution to a small flask that is equipped with a reflux condenser. Cool to 0° C. and add slowly through the top of the condenser 13.7 g. of benzenesulfonyl chloride. Allow to stand for a short time and filter. Wash with ether and dry in a desiccator. Recrystallize by dissolving in alcohol and then precipitating by adding 2 volumes of ether.[2]

Tetramethylammonium hydroxide: Dissolve 40 g. of pure dry tetramethylammonium chloride in 80 ml. of absolute methyl alcohol, and mix with 83.8 g. of a methyl alcohol solution containing 20.4 g. of potassium hydroxide. Allow to stand 1.5 hours at room temperature, and filter with slight suction through a Buchner funnel. Wash with a few ml. of methyl alcohol. Add about 45 ml. of water to the filtrate, and distill under reduced pressure on a water bath at 35° C. After two hours, add to the residue in the flask 35 ml. of water and continue the distillation for 1 hour. Transfer the solution in the flask to a crystallizing dish with a ground overlapping lid. Cool and collect the crystals of the pentahydrate. An additional quantity of the reagent may be obtained by leaving the filtrate for several days in a desiccator.[3,4]

Determination of magnesium. Tetramethylammonium hydroxide may be used for the precipitation of magnesium hydroxide, but does not appear to be as satisfactory as piperidine or sodium hydroxide.[5]

Determination of sodium and potassium and lithium. Portnov and Afanasev [6] have determined sodium in potassium chloride, carnallite and sylvinite by first precipitating the potassium with magnesium hexanitrodiphenylamine, and then determining sodium in the filtrate polarographically in the presence of phosphoric acid and an excess of tetramethylammonium hydroxide by the method of Majer.[7]

Zlotowski and Kolthoff [8] have studied the use of tetramethyl- and tetraethylammonium hydroxides as supporting electrolytes in the determination of the alkali metals, and they conclude that the tetraethyl compound is the more satisfactory.

1. *Organic Synthesis,* Collective Vol. I, 2nd ed., p. 528, John Wiley, New York (1941).
2. L. W. Jones and H. F. Whalen, *J. Am. Chem. Soc.* **47**, 1343-52 (1925).
3. J. Walker and J. Johnson, *J. Chem. Soc.* **87**, 957-61 (1905).
4. W. Weith, *Ber.* **8**, 460 (1875).
5. L. H. Borgstrom, *Hyllningsskrift tillagnad Ossian Aschan.* 118 (1920); *C.A.* **16**, 2091 (1922).
6. M. A. Portnov and S. K. Afanasev, *Zavodskaya Lab.* **7**, 421-5 (1938); *C.A.* **33**, 78 (1939).
7. V. Majer, *Z. anal. Chem.* **92**, 321-51 (1933); *C.A.* **27**, 2902 (1933).
8. J. Zlotowski and I. M. Kolthoff, *Ind. Eng. Chem., Anal. Ed.* 14, 473-4 (1942); *C.A.* **36**, 4437 (1942).

TRIMETHYLPHENYLAMMONIUM CARBONATE

$C_{19}H_{28}O_3N_2$ Mol. Wt. 332.41

$$[(CH_3)_3C_6H_5N]_2CO_3$$

Use: Determination of zinc.

Determination of zinc. When zinc is precipitated with sodium carbonate, the precipitate is contaminated with sodium, probably as the zincate. The error due to this source may be eliminated by using trimethylphenylammonium carbonate as the precipitant.[1]

1. E. Schirm, *Chem.-Ztg.* **35**, 1177, 1193-94 (1911); *C.A.* **6**, 330 (1912).

TETRAMETHYLAMMONIUM IODIDE

$C_4H_{12}NI$ Mol. Wt. 201.03

$$(CH_3)_4NI$$

Use: Detection of germanium.

Tetramethylammonium iodide is a crystalline solid. It is slightly soluble in cold water and absolute alcohol, but is insoluble in ether.

Preparation: The compound is prepared by the action of trimethylamine on methyl iodide. The product is purified by recrystallizing from alcohol or ethylacetate.

Detection of germanium. Germanium can be detected by the white crystalline precipitate which forms when a solution of germanium hydroxide, $Ge(OH)_2$, in hydroiodic acid is treated with a 10 per cent solution of tetramethyl ammonium iodide. The compound formed is $(CH_3)_4NI \cdot GeI_2$.[1]

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1. T. Karantassis and L. Captos, *Compt. rend.* 201, 74-5 (1935).

TRITON B

Use: Separation of magnesium from sodium and potassium.

Krokovski [1] has used triton B for the separation of magnesium from sodium and potassium. Triton B is obtained as a yellow, bitter liquid from Rohm and Haas of Philadelphia. The reagent is a solution of an organic quaternary ammonium base. This solution has a normality of about 2.5, a sp. gr. of 1.0579, and the molecular weight appears to be about 170.

The reagent serves for the quantitative precipitation of magnesium hydroxide in the presence of sodium and potassium, and, after filtration, sodium and potassium may be detected in the filtrate. The reagent is also useful in the qualitative analysis of magnesium, since the precipitation may be effected at the boiling point without the previous removal of ammonium salts. The most satisfactory procedure in such cases is to add the reagent in small portions and follow by boiling the solution.

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1. T. Krokovski, *Z. anal. Chem.* 112, 183-6 (1938); *C.A.* 32, 4464 (1938).

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Determination of Cyanate

semicarbazide hydrochloride, 454

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β-naphthylamine, 414
phthalic acid, 77
quinoline-8-carboxylic acid, 219
salicylic acid, 125
sulfondiacetic acid, 228
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benzidine, 290
citric acid, 105
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α-naphthylamine, 411
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aniline, 271
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ethyl acetate, 240
formic acid, 37
phenylhydrazine, 444
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benzylamine, 330
dimethylaniline, 351
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5-bromo-2-aminobenzoic acid, 203
citric acid, 104
ethylenediamine, 385
formic acid, 39
guanidine carbonate, 388
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tartaric acid, 181
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α-naphthylamine, 409
safranine, 453
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benzidine, 320
citric acid, 105
3,5-diaminobenzoic acid, 336
2,4-diamino-6-hydroxypyrimidine, 340
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m-phenylenediamine, 432
p-phenylenediamine, 438
safranine, 453
salicylic acid, 127
succinic acid, 88
sulfanilic acid, 458
tartaric acid, 184
m-toluidine, 480
o-tolidine, 476
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Determination of Nitrite

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Determination of Oxygen
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diethylamine, 346
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diethylamine, 346
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Determination of Silicon
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Determination of Sulfate
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α-naphthylamine, 411
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tartaric acid, 184
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Determination of Thiosulfate
ethylenediamine, 386

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benzylamine, 330
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fumaric acid, 42
m-nitrobenzoic acid, 225
oxalic acid, 61
phenylhydrazine, 446
salicylic acid, 127
sebacic acid, 81
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Detection of Thulium
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Determination of Tin
oxalic acid, 62, 64
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α-naphthylamine, 410
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Determination of Uranium
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dianisidine, 342
diphenylamine, 365
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p-phenetidine, 425
phenylanthranilic acid, 209
o-phenylenediamine, 431
p-phenylenediamine, 436
salicylic acid, 126
tannin, 145
tartaric acid, 183
o-tolidine, 470
1,2,5-toluylenediamine, 483
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diphenylamine, 365
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Determination of Water

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succinic acid, 88

Detection of Ytrium

aluminon, 100
aurin tricarboxylic acid, 100
oxalic acid, 61
succinic acid, 88
tannin, 170

Detection of Zinc

1-aminoanthraquinone-2-carboxylic acid, 188
α-aminopyridine, 261
aniline, 264
anthranilic acid, 201
benzidine, 277
2,7-diamonofluorene, 339
diethylaniline, 347
diphenylamine, 366
diphenylbenzidine, 374
p-phenetidine, 428
phthalic acid, 77
triethanolamine, 485

Determination of Zinc

anthranilic acid, 194, 197
5-bromo-2-aminobenzoic acid, 203
chloroacetic acid, 91
2,7-diaminofluorene, 339
dimethylamine, 350
formic acid, 35
guanidine carbonate, 388
lactic acid, 111
morpholine, 399
5-nitroquinaldic acid, 206
oxalic acid, 56
palmitic acid, 75
quinaldinic acid, 214
sulfosalicylic acid, 137
tartaric acid, 183
trimethylphenylammonium carbonate, 511

Detection of Zirconium

aluminon, 100
aurin tricarboxylic acid, 100

Determination of Zirconium

acetic acid, 15
aniline, 262
benzylamine, 330
dimethylaniline, 351
phenylhydrazine, 446
tannin, 152, 168, 169
tartaric acid, 181
o-toluidine, 480
xylidine, 500